BLEACHING

AND RELATED PROCESSES

As Applied to Textile Fibers
and Other Materials

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PREFACE

In the present volume I have attempted to bring together under one subject a discussion of the main facts relating to the bleaching of a variety of materials, with the idea that the processes of bleaching are, in themselves, general enough in character to be susceptible of this treatment. On this account, the classification I have adopted is one based on the materials to be bleached rather than on the bleaching agents themselves. In the first rank, of course, come the textile fibers, and among these the one of preeminent importance is cotton. So much is this the case, indeed, that when the term "bleachery" is used in general *parlance,* the invariable meaning is one devoted to the bleaching of cotton. This will account for the relative amount of space and consideration given to the different topics contained in this volume. I have attempted to preserve a proper balance of the subject matter in recognizing the respective values of the different provinces of bleaching. Naturally, therefore, a much larger space is given to cotton bleaching than to any other branch.

Inseparably bound up with the actual process of bleaching itself are certain correlated preliminary and subsequent processes which must also receive due consideration. In wool and silk bleaching, for instance, the preliminary scouring or degumming operations are of even more importance than the final whitening of the fiber. In cotton bleaching the previous boiling-out is in reality the chief essential in the complete process. This will account for the rather detailed and exhaustive discussion given to the subjects of scouring wool, degumming silk and boiling-out cotton.

The classification of the subject with respect to the materials to be bleached has been adopted for the purpose of giving the reader a clearer understanding of any one topic as a whole. I take it for granted that the average reader of such a volume as the present one will be more interested in viewing a complete survey of wool bleaching, of linen bleaching, or whatever the topic may be, than in an academic discussion, for instance, of the peroxide method of bleaching in general. While this system of classification is by far the most practical one from the point of view of the reader, it possesses the technical defect of a certain, yet unavoidable, amount of repetition, especially where practically the same process of bleaching is used for different materials. In order to preserve the unity of the topic under consideration, however, I have not hesitated to repeat processes that may have been previously mentioned with only minor differences of detail, as I have considered it better to do this than to risk the more serious charge

of incompleteness or to involve the inconvenience of continued reference.

Illustrations and diagrams have been liberally employed in this volume, chiefly for the purpose of enabling the reader to visualize more clearly the processes under discussion. These illustrations have been selected and placed with reference to the development of the text, so that as the reader studies the text he may have before his eye the particular machine or apparatus relating to the subject. The distribution of these illustrations has been made with reference to chapters, as owing to the exigencies of typographical make-up it is not always possible to insert the illustration at the exact psychological position of the text. Furthermore, I have purposely avoided giving dry details of mechanical descriptions relating to the machines illustrated, as I do not believe that the reader is either instructed or entertained by including these mechanical details that savor more of a trade circular or a patent specification.

This volume has been written primarily for the textile chemist and the actual operative in the mill, so that the subject has been approached more from the practical point of view than from that of the theoretical and academic chemist. To this end I have avoided sprinkling the pages with complicated chemical formulas and equations, and have sidestepped the high-brow disquisitions of physical chemistry and mathematical physics by which many chemical books seek to mystify and awe the reader into the belief that they are acquiring a scientific vision. Science is nothing more than classified common-sense, and in presenting this contribution to the science of bleaching, I have merely attempted to classify and coordinate the common-sense facts underlying the industry. The technique of the subject is presented rather than a metaphysic of hypothetical causes or a scholastic logic of chemical formulas.

This book is an outgrowth of over twenty years' practical experience of the author as a textile chemist occupied very largely in the problems of bleaching, and naturally it will be found that those subjects will be the greater stressed the more they lie within that experience, while other subjects have been perhaps not so fully dealt with where reliance has had to be placed mostly on the published literature; but this I believe is a shortcoming common to all books on technical subjects.

While the main theme herein is that of textile bleaching and scouring, there is also included a discussion of the topic of bleaching as extended to other fields of industry. As these fields, as a rule, have not been subjected to any degree of scientific investigation or method, they can be dealt with in only a comparatively sketchy and inadequate manner. I realize these limitations, but hope that this publication may serve as an incentive towards an increased interest in these fields and that students will recognize them as interesting possibilities for fruitful research.

As to the practical bleacher and the responsible executives of this industry, it is to be hoped that this volume will help towards inciting an interest in the systematic investigation and scientific study of actual

mill processes and operations. Most bleacheries are overgrown with the moss of secrecy, prejudice and tradition, and harnessed to rule-of-thumb methods that have been evolved from primordial ancestral experience. That such experience is the basis of many useful ideas and satisfactory methods of operations is not to be gainsaid; but at the present time unless such experience is analyzed in the light of modern scientific knowledge it may come to be a retarding influence rather than a progressive one.

As a further explanation of the scope of this volume it may be said that it is limited to the direct subject of bleaching and the necessary preliminary operations connected therewith. The discussion of finishing operations on bleached fabrics (especially with reference to cotton goods) has been purposely avoided, as to deal with these adequately would have led me too far afield from the main theme, and would have made the volume out of proportion and would have destroyed its unity of purpose. While it is true that the finishing of cotton goods is intimately bound up with the bleaching thereof, and that bleaching, perhaps, is to be considered merely as one of the processes in finishing, nevertheless it has not been possible or feasible to include these matters in the scope of the present volume.

J. Merritt Matthews.

New York City,
June, 1921.

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BLEACHING

Chapter I.

Introduction.

1. The Raw Textile Fibers.

The textile fibers in their condition as raw materials contain considerable amounts of impurities which have to be removed in order to render the fiber serviceable for manufacturing purposes. Wool, for example, as it occurs in the fleece of the sheep, contains a large quantity of greasy matter and dirt; the silk fiber, though comparatively free from foreign matter, is enveloped by an integument of a glue-like substance; cotton, though pure in comparison with wool, is nevertheless contaminated with a small amount of matter other than true fiber; and the other vegetable fibers usually have quite a large amount of associated foreign matter. In addition to this, all of the textile fibers have a small quantity of natural coloring matters as a composite part of their substance which is necessary to remove when a pure white fiber is required.

The removal of grease, dirt, or other extraneous matter is an operation which naturally falls under the general term of *scouring;* although this expression is more especially given to the cleansing of wool alone, the scouring of cotton being spoken of as *boiling-out,* and the scouring of silk as *boiling-off, stripping,* or *degumming.* The removal or destruction of the natural coloring matters in the fiber is the real province of *bleaching* Inasmuch as it is always necessary to cleanse the fiber thoroughly before bleaching, a preliminary scouring operation must always be considered.

Owing to the fact that raw wool contains such a large amount of foreign matter, and owing also to the greasy character of the latter, it is almost impossible to carry the fiber through any of the manufacturing operations without a preliminary scouring; even previous to the dyeing of loose wool, the stock must first be cleansed. There are rare instances of wool being carded and spun in the greasy, unscoured condition, and also similar instances of the stock being dyed in such a condition, but these are exceptionable cases and constitute but a small portion of the wool ordinarily manufactured; and even under such conditions, the wool has been considerably cleansed by washing while still on the sheep.

From the nature of the impurities on silk, this fiber may be carried

through a variety of operations and even be dyed without first removing to any extent the silk-glue, but the high luster and softness of the fiber are not developed until it has been scoured.

Cotton, as already mentioned, has but a small amount of foreign matter other than pure fiber; hence, this does not, as a rule, interfere with the manufacture and dyeing of the stock. In fact, owing to the waxy-like nature of the majority of the impurities on the cotton fiber, they are a help rather than a drawback to the carding and spinning of the material; owing to their water-repellent nature, however, they stand in the way of the proper dyeing of the stock, in so far as not to allow of the free transpiration of solutions through the fiber. In the bleaching of cotton, however, it is absolutely essential to thoroughly scour the fiber in order to obtain satisfactory results.

In many of the other vegetable fibers the stock cannot be obtained in a white condition without more or less disintegration or weakening of the individual filaments. Linen or jute, for instance, cannot be bleached to a pure white without very serious detriment to its strength. This is caused by the fact that these textiles are prepared from what are known as *bast fibers* and the commercial fibers are composed in reality of bundles of small fibrils held together by an intercellular tissue. To obtain perfect bleaching, ordinarily, this tissue must be removed, hence the fiber becomes more or less decomposed into its fibrils and is necessarily weakened. Due to this fact, many of these fibers are not scoured and bleached, but are used in their natural color.

2. Natural Pigments in Fibers.

All of the textile fibers, whether of vegetable or animal origin, possess more or less coloring matter or pigment in their composition. Wool, in common with its cogenor, hair, is known to exist in a number of colors, varying from a pale yellow to a deep brown, or even a black. Even ordinary "white" wool has a slight yellow tint after scouring, due to the presence of a natural organic pigment in the fiber.

Silk also possesses coloring matters which impart to it a slight brownish yellow tint, which in some varieties is quite pronounced when the silk is still in the gum or raw state; the majority of this coloring matter, however, is merely present in the sericin, or layer of silk-glue, which covers the fiber proper, so that when this layer is removed by boiling-off the fiber comes up fairly white. In many wild silks, however, the amount of pigment-matter in the fiber itself becomes quite pronounced, and gives to the silk a marked brownish color.

Cotton, even after a thorough boiling-out for the purpose of removing external impurities, still retains a slight brownish yellow color, and some varieties, such as Nankin cotton, have quite a deep brown color.

Linen or flax will vary much in the quality and quantity of the coloring matter present, according to the method by which the fiber is prepared from the plant; the fiber itself has but little natural pigment, but it becomes more or less stained in the retting process by the coloring matters extracted from the rest of the plant; the result is that linen, as it usually appears in trade, is of a grayish brown color.

Other vegetable fibers, such as jute and hemp, are, as a rule, rather deeply colored, though ramie is remarkably white. With regard to these bast fibers, the amount of coloring matter present is usually in proportion to the amount of alteration products of cellulose present in admixture with the true cellulose.

In the large majority of instances in dyeing, the presence of the natural coloring matters of the fiber is not appreciably harmful to the color to be produced by the dyestuff. When delicate shades and tints, however, are desired, or when it is required that the fabric be left undyed and in a white condition, it generally becomes necessary to remove the natural coloring matter from the fiber by some chemical treatment. The process by which this is accomplished is termed *bleaching,* and the word really means to "whiten." [1]

3. Tinting.

The destruction, or removal, of the natural coloring matters in the textile fibers may be brought about by a variety of methods. In certain cases, it is only necessary to tint the material with a complementary color to that already present; and as this latter is usually a yellow or a yellowish brown tint, the complementary tint would be blue or violet. The complementary tints combining to give the effect of one color produce a neutral gray, to which the eye is far less sensitive than it is to either of the complementary or component tints; and, in consequence, the material so tinted appears to the eye to have much less color; or, in other words, appears whiter. In this method of bleaching there is no actual destruction of the natural coloring matter or pigment, and there is in reality more actual color present in the fiber after tinting than before, only it is not so apparent to the eye. Very small quantities of such dyestuffs as Methyl Violet, Indigo Extract, Acid Violet, Ultramarine, etc., may be employed for the purpose of tinting, and must be used with a due regard to proportion, otherwise the material may be given a bluish or violet tone as perceptible as the yellowish tint which existed before. The majority of these tints, however, are not at all permanent to the action of washing and exposure, and in consequence are gradually removed, with the result that the original yellowish color once more becomes apparent as the complementary tint fades away. This method of bleaching by the tinting process can only be successfully applied in cases where the amount of the original natural coloring matter is very small; for if this is too pronounced the amount of blue or violet complementary color required to overcome it will be proportionately larger, and the resulting neutral grayish tone may become so pronounced that the material after tinting will exhibit a dirty or muddy appearance. Nor is this method of bleaching applicable to material which it is desired shall possess a permanent white color; it is often employed, however, for the purpose of giving bleached goods a whiter appearance in the store so as to render them more salable.

Tinting, however, is nearly always employed as a finishing operation

[1] In its etymological sense, the word "bleach" means to whiten or make pale. It is apparently derived from the Anglo-Saxon *blecan,* to fade, and we also have the German *bleichen,* to whiten, and the French *blanchir* of the same meaning.

in nearly every process of actual bleaching; in such cases it is for the purpose of giving the bleached white a bluish cast which is more agreeable to the taste, as a rule, than a full dead white. The tinting under these circumstances is generally done with a minute quantity of violet or blue coloring matter. It livens up the appearance of the bleached white and gives it a fresh and bright finish.

A variety of coloring matters are employed for the purpose of this tinting; Acid Violet and Victoria Blue are largely used, as are also Ultramarine, soluble forms of Prussian Blue and the fast vat blues, such as Indigo, Indanthrene Blue, etc.

4. Chemical Bleaching.

Bleaching, in the proper sense of the term, implies an actual removal or destruction of the natural pigment in the fiber, and not merely a temporary neutralization of its color effect by tinting with complementary colors. The coloring matters existing in the raw fibers are of organic origin; that is to say, they are not mineral compounds. Being of this nature they are peculiarly susceptible to the action of various chemical agents of both a reducing and oxidizing character. It is on these facts that the two processes of bleaching at present in vogue depend for their efficiency. The one, which is used almost exclusively in connection with the animal fibers, involves the use of a strong reducing agent, such as sulfurous acid, sodium hydrosulfite, etc.; the other process employs a strong oxidizing agent, such as hypochlorous acid (or its salts), which finds use in connection with the vegetable fibers, or hydrogen peroxide, which may be employed in connection with all fibers.

5. Reduction Process.

In the reduction process of bleaching, which is employed principally for wool, the coloring matter does not appear to be ultimately destroyed, but the bleaching effect is accounted for on the theory that the organic pigment is either reduced to some colorless compound by the general reducing action of the bleaching agent, or it may form a colorless derivative with the sulfurous acid itself. It is not considered probable that the pigment is chemically decomposed in such a manner as to be utterly destroyed, for if this were the case, the bleaching effect would be of a permanent character; but as it is observed that the yellowish tint of wool gradually returns on exposure to the air when bleached by means of sulfurous acid, it has been supposed that the coloring matter has not been really destroyed, otherwise it could not again be generated in the manner observed. Examples of the decolorizing action of sulfurous acid have been observed in connection with many dyestuffs; for instance, a solution of Magenta is rapidly decolorized when treated with this reducing agent; and it has been shown in this case that the coloring matter has not been destroyed, but is only converted into a colorless compound consisting of a reduced derivative of Magenta known as rosaniline. This reaction has also been extended to many other coloring matters. Again, certain other dyestuffs, such as

Alizarine Blue S, have been shown to form a chemical compound with sulfurous acid which is both colorless and soluble. In view of these chemical reactions, the above theory as to the effect of sulfurous acid on the coloring matter in wool has been suggested.

The same remarks which have been applied to the return of the yellowish tint of wool which has been bleached with sulfurous acid,

FIG. 1.—Grassing of Linen in Old England.

may in like manner be applied to this same action with respect to silk, straw, or other fibers, which may have been bleached by the same reagent; for it is observed that in each case exposure of the bleached material to the air will result in the gradual return of the yellowish color which it was the object of the bleaching to remove.

In contradistinction to these explanations, however, it may be said that the yellowish tint does not appear to be restored to wool bleached

with sulfurous acid when treated with mild oxidizing agents, such as dilute solutions of chloride of lime, potassium permanganate, hydrogen peroxide, etc. If it were a fact that the bleaching-out of the natural pigment were due to its being reduced to a colorless compound, and that the gradual restoration of the original color were due to a reoxidation of this derivative to the parent substance again by the action of the atmosphere, this reoxidation should take place much more rapidly when brought in contact with such oxidizing influences as above suggested. But as this does not take place we must be somewhat sceptical in accepting such an explanation. If, on the other hand, the bleaching effect were due to the formation of a colorless compound of the pigment with the sulfurous acid, it would seem probable that if the latter constituent of the compound were removed the original pigment might be destroyed in the presence of even diluted or mild oxidizing agents, whereas the influence of the atmosphere might have a somewhat different effect.[2]

This explanation receives a further support in the fact that however well wool may be washed after bleaching with sulfurous acid, it seems impossible to remove absolutely all of the latter compound from the fiber, evidently suggesting some form of chemical combination of the sulfurous acid with either the wool itself or some of its constituents.[3] On long exposure this compound may be broken down, with the result that the pigment is again liberated in its original condition. But we also have to meet an objection in this theory similar to that advanced against the former one. By treatment with mild oxidizing agents already described the traces of sulfurous acid which are left in the wool after bleaching are totally removed by reason of the conversion of the sulfurous acid into sulfuric acid. The removal of the reducing agent, however, does not appear to cause the natural pigment to be reformed, as would be expected. This action of oxidizing agents on the sulfurous acid compound may be more complicated, however, and as indicated above may lead to the destruction of the pigments.

Another point which also has a bearing on this question is the fact that wool which has been bleached by means of hydrogen peroxide, whereby the coloring matter is supposed to be completely destroyed, appears to evince as much affinity for sulfurous acid as does unbleached wool itself; consequently, it cannot be said that the combination of the sulfurous acid is one totally confined to the pigment matter in the fiber.

Another explanation which may be offered to account for the return of the yellowish tint to wool bleached with sulfurous acid when

[2] Of course, we must also bear in mind the possibility that the yellowish tint reappearing on the bleached material is a coloring matter of quite a different nature than that originally present in the fiber, and may be caused by the development of other chemical bodies by the influence of atmospheric oxidation or exposure. Our knowledge of the subject is still uncertain and inexact, and is a fit subject for further chemical research

[3] The older theory that the coloring matter of wool was decomposed by reduction through the action of sulfurous acid has been considerably discredited by the investigations of Harpf (*Farber-Zeit.*, 1905, p. 88), who shows that the formation of sulfuric acid cannot be detected either in the wool or in the wash waters. We also know that in only very isolated cases are dyestuffs decomposed by sulfurous acid, but, on the other hand, tend to form colorless combinations with the acid which, for the most part, are soluble in water, weak alkalies or soap solutions.

traces of the reducing agent are not entirely removed from the fiber by chemical treatment, is that the sulfurous acid has formed some chemical compound with the substance of the wool fiber itself, which gradually undergoes decomposition leading to the formation of yellowish products. This view of the subject would account for the return of the color to the wool, and would also account for the fact that the removal of the sulfurous acid by proper methods of oxidation leaves the wool in a permanently bleached condition.

6. Oxidation Process.

By the oxidation process of bleaching it is supposed that the coloring matter in the fiber is chemically decomposed in such a manner as to be incapable of being subsequently reformed; consequently there is no danger of the color reappearing after the material has once been bleached. The oxidation method has long been employed in connection with vegetable fibers, hypochlorous acid in the form of some of its salts, such as sodium hypochlorite or chloride of lime, being used as the oxidizing agent. The use of such chlorine compounds apparently does not depend on the action of chlorine itself on the coloring matter, but is due to the action of chlorine on the moisture present, whereby oxygen is liberated in the nascent condition. It is this latter agent which really accomplishes the destruction of the pigment. This is evidenced by the fact that dry chlorine gas apparently has no action on the organic pigment in vegetable fibers, but in the presence of moisture, the effect of the chlorine becomes at once noticeable. Chlorine compounds may not be employed in connection with wool or silk, as the animal fibers combine chemically with the chlorine itself, giving rise to yellow products; so that wool, for instance, after being treated with chlorine or its compounds, is of a deeper yellow color than before the treatment.

Bleaching by means of oxidation may also be carried out by the use of certain peroxides, such as hydrogen peroxide, sodium peroxide, and potassium permanganate. The last substance corresponds to a peroxide in the sense that it contains a relatively large proportion of oxygen in its composition, and so united as to be capable of liberation very readily. Of these substances, sodium peroxide is the one mostly employed at the present time. It possesses neither the uncertainty of the sulfurous acid bleach nor the disagreeable features of the chlorine bleach, and, in addition, may be used in connection with all classes of fibers. Its bleaching properties are due to its capability of easily liberating nascent oxygen in immediate contact with the substances to be bleached.

7. Minor Processes.

Other forms of bleaching have been proposed from time to time. Some, which depend indirectly on the use of the electric current, like the electrolytic process, prepare a solution of sodium hypochlorite simultaneously with the bleaching action; a current of electricity being passed through a solution of sodium chloride, whereby sodium hypo-

chlorite is formed, and this serves as the bleaching bath. The use of electricity has also been suggested as a means of rendering chlorine gas more effective in its bleaching qualities; the gas being conducted through an apparatus provided with two electrodes between which an electric spark is continually passing. This treatment is supposed to decompose the chlorine molecules into a simpler atomic condition, whereby their chemical affinities become more active; but this method has never yet been introduced into practice, and grave doubt exists as to whether or not the electrification of the chlorine increases the bleaching efficiency of that compound. Potassium permanganate has also been employed as a bleaching agent in connection with sodium bisulfite, and very satisfactory results have been obtained, though the method is generally more expensive than the other processes in more general use. Ozone has also been used as a bleaching agent, but its high cost of production is prohibitive to general practice, and it has also been found that ozone exerts a seriously destructive action on the textile fibers when employed in concentrations sufficient to be effective in bleaching.

8. Theory of Bleaching.

Since all of the bleaching compounds acting under the oxidation method rely for their bleaching effect on the final liberation of oxygen either from the compounds themselves, or through the decomposition of the moisture which must be present, the question would naturally arise as to why oxygen itself would not be a useful bleaching agent. There have been attempts made to employ oxygen in the free state as a substitute for chlorine and its compounds, but such experiments have not been attended with any degree of success with the exception of where the free oxygen is used in connection with sunlight, as in the "grassing" of linen. The explanation to be given as to why free oxygen of itself is not an active bleaching agent probably is that in its ordinary condition oxygen gas exists in a molecular state; that is to say, two atoms of oxygen are joined together to form a comparatively stable molecular compound in which the chemical activity of the oxygen atom is more or less neutralized. When acted upon by sunlight, however, in the presence of moisture, the oxygen molecule is probably split up into the atomic condition in which its chemical activity is greatly increased. This is also true of the oxygen which is formed in the various chemical reactions of bleaching, where it is liberated from its compounds, or indirectly by the bleaching agent from water; in these cases the oxygen which acts upon the material to be bleached is in the atomic condition at the moment of its liberation, or the so-called "nascent" condition.

In experiments relating to the bleaching of paper-pulp,[4] which were also extended, however, to the bleaching of the jute fiber, it has been stated that when a stream of oxygen gas is passed into a solution of chloride of lime, the bleaching efficiency of the latter is much increased, in fact the saving in the amount of chloride of lime necessary is stated

[4] Thorne, *Jour. Soc. Chem. Ind.*, 1889, p. 82.

as being about 40 to 50 percent. With solutions of chlorine, oxygen also acts in the same manner, and when a mixture of the gases is conducted into water a considerable quantity of the oxygen appears to be absorbed, while the bleaching efficiency of the chlorine is raised 50 percent. The action of the oxygen in such cases may be that it reacts with the chlorine to form oxides of chlorine and perhaps free ozone, thus increasing the bleaching activity. It is somewhat remarkable, however, that if a solution of bleaching powder through which a current of oxygen gas is being passed is titrated with arsenious acid, the amount of the latter reagent is not increased. Probably the *raison d'être* of the action of the oxygen must be sought for in the chemical behavior of the coloring matters which are bleached; that is to say, in the difference in the effect of chlorine and oxygen on them. Reference has been made in a preceding paragraph to the method of increasing the efficiency of chlorine gas as a bleaching agent by passing it through an electric discharge; it may be that this increased efficiency, if any, may be due to the formation of ozone through the action of the electric spark on the accompanying oxygen, and the mixing of this with the chlorine.

9. Historical.

The art of bleaching by chemical methods does not date back to more than comparatively recent times. The methods employed in antiquity, and even in more modern times, depended principally on the action of light and air on the coloring matters which it was desired to remove. It may also be said that bleaching, in the proper sense of the term, was almost entirely limited to the vegetable fibers, such as linen and cotton, as wool and silk were considered to be sufficiently white for all purposes, and only required a simple scouring operation.

Pliny gives a description of the method employed by the ancient Gauls for the cleansing and whitening of their textile fabrics; they made use of an alkaline substance known as lixivium, which was extracted from the ashes of burnt wood or other vegetable matter, and also apparently employed this alkali in combination with oils in the form of soaps. The fumes of burning sulfur (sulfurous acid) were employed for the purposes of bleaching at a much later date, and it was not until the latter part of the eighteenth century that chlorine and its compounds became known as bleaching agents.

The primitive methods of bleaching (confined more especially to linen, as cotton was considered white enough for all general purposes) required the exposure of the cloth on large grassy meadows for a considerable period of time. This necessitated not only the expenditure of a vast amount of labor and time, but also the expense of land rent and the care of the bleaching fields was considerable. In the early part of the eighteenth century extensive bleaching fields were established in Ireland for the bleaching of linen. In the Irish method the alkaline liquors obtained from the ashes of sea-weed (kelp) were used for steeping and boiling the cloth. The steeping process usually occupied several days, after which the linen was thoroughly washed and

spread out on the grass for a period of several weeks. The steeping or boiling in the alkaline liquors was known as "bucking" or "bowking," and the exposure on the grass was called "crofting." In order to obtain a satisfactory bleach, these two processes were alternately repeated, often five to six times. After exposure on the grass, the linen was steeped for several days in sour milk, then washed clean and again spread on the grass.

Before bleaching was taken up as a national industry in Ireland, it was practiced principally in Holland, and up to the middle of the

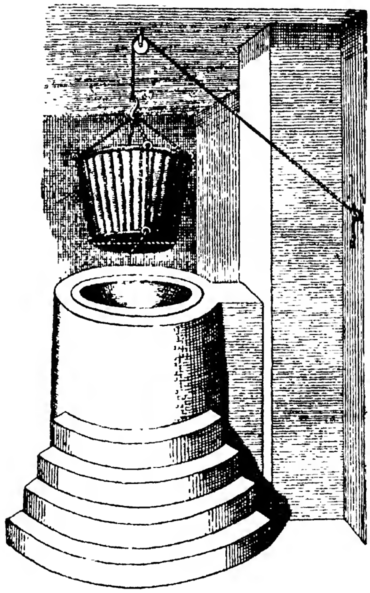

Fig. 2.—Showing Antique Method of Boiling-out.

eighteenth century it could almost be said that the Dutch held a monopoly of the bleaching trade for the rest of Europe, including also the majority of the linens manufactured in the British Isles. This transfer of the cloth from England to Holland and back again, together with the time required for bleaching, occupied a period of about six months.

Bleaching in Holland was conducted, for the most part, in the neighborhood of Haarlem, and the method consisted in a general way as follows: The linen was first steeped in a weak lye, and then in a hot potash lye for about a week; after this it was given a thorough washing, and then steeped in buttermilk for several days.[5] An exposure in a moistened condition on the grass for the several months of

[5] The function of the buttermilk was to act as a "sour" or acid bath, the effective agent being the lactic acid present in the sour milk.

summer followed, and completed the bleaching operation. The action of sour milk in bleaching was evidently due to its acid constituents, which rendered the impurities in the linen more soluble. This beneficial action of acids was realized by Dr. Home of Edinburgh, who showed that by substituting a dilute solution of sulfuric acid for the sour milk, better results could be obtained and at less expense. The treatment with dilute sulfuric acid for 24 hours gave as good results as steeping in sour milk for a week or more. Even with this improvement, however, the proper bleaching of linen goods required a period of four to six months.

The Swedish chemist Scheele discovered chlorine in 1774, but it was not until 1785 that the bleaching properties of this gas were studied with reference to their commercial application. Berthollet was the first chemist to point out the commercial possibilities of chlorine as a bleaching agent for linen and cotton materials. An aqueous solution of the chlorine gas was used, and the goods were passed through the hot solution; but it was a number of years before the proper method of using the new bleaching agent was learned, and it did not come into general practice or favor until an alkaline solution of the gas was employed. This led to the discovery by Tennant, of Glasgow, that lime-water saturated with chlorine gas gave a very effective bleaching liquor. Tennant patented his process in 1798; but several years later he was prevented from reaping any material benefits from it by a legal decision against the validity of the patent. This process revolutionized the methods of bleaching, and cut down the time required from several months to a couple of days, or even less. Tennant, a few years later, was successful in manufacturing a dry chloride of lime or bleaching powder (as it was then called, and which name it has still retained), obtained by saturating quicklime with chlorine gas. This preparation rapidly came into favor as the principal bleaching agent for linen and cotton goods.

The next steps in the direction of improving the methods of bleaching, both with respect to the quality of the goods and the time consumed in the process, was the introduction of suitable machinery to supplant manual labor. This led to a greater simplification of the processes employed and a more economical use of the various chemicals needed. The so-called "American Process" came into vogue about 1837, and with minor improvements, is still the method in general practice. In brief outline, this process consisted of singeing, washing, boiling under pressure with lime, souring with weak acid, boiling under pressure with alkali and resin soap, steeping in a solution of bleaching powder, souring again with weak acid, and finally washing, tinting and drying.

Lime has been used since antiquity for the purpose of boiling out linen and cotton previous to bleaching, and on account of its efficiency and cheapness, it has always remained more or less in favor. In the middle ages, bleachers avoided its use owing to its liability to injure the fabrics; this was likely due to the absence of an acid treatment for the purpose of removing the excess of lime from the fiber.[6]

[6] For a good résumé of the history of bleaching, see the *Textile American*, Vol. III, Nos. 3, 4, and 5.

Chapter II.

The Wool Fiber and Its Impurities.

1. General Considerations.

The quantity of pure wool fiber existing in the fleece as it is sheared from the sheep will amount to only from 25 to 70 percent of the total weight of the fleece.[1] The quality of the fiber will have much to do with this amount; that is, if the wool consists of fine staple fiber, such as full bloods, merinos, etc., it will contain a relatively larger amount of foreign material than a wool consisting of coarse stapled fibers, such as Territory, Lincoln, etc. This is due to the fact that the amount of grease exuded from the skin of the sheep into the fleece is greatly conditioned by the number of hair fibers growing on a definite area of the skin, for the sebaceous glands in the skin which secrete the greasy substances are located around the hair follicle, or root of the fiber; and hence, the more fibers per square inch of skin surface the greater will be the number of the sebaceous glands, and consequently the greater amount of grease exuded. The same condition is true of the amount of perspiration which is thrown off as waste tissue by the sheep through the sudorific glands in the skin. Hence, it is readily seen that the finer the fiber, or in other words, the greater the number of fibers growing on the skin, the greater will be the quantity of grease and dried-up perspiration which will eventually be deposited on the

[1] In English practice the following are the average proportions of impurities in various wools:

	Percent
Long English wools	30
Medium cross-bred	40
Merino wools	55 to 60

According to the most eminent authorities the following represent an approximate analysis of the constituents of the average classes of greasy wools:

	Grease Percent	Dirt Percent	Clean Wool Percent
Greasy Merino	40	15	45
Greasy Crossbred	35	10	55
Greasy Luster	20	10	70
Heavy Greasy Merinoes	26	40	34
Medium "	15	25	60
Light "	5	15	80

Fleeces show considerable variation viz., moisture, from 4 to 24 percent; grease, from 12 to 47 percent; dirt, from 3 to 24 percent, and clean fiber, 15 to 72 percent. For commercial purposes the following table is of use.

Wool	Shrinkage Percent	Yield Percent
Merinos	40 to 70	60 to 30
Fine crossbred	25 " 45	75 " 55
Medium "	25 " 35	75 " 65
Strong "	20 " 25	80 " 75
British down wools	20 " 30	80 " 70
" medium "	20 " 25	80 " 75
" luster "	15 " 25	85 " 75
" demi-luster wools	15 " 25	85 " 75

fleece. Furthermore, the amount of sand, dirt, vegetable matter, burrs, etc., which the fleece will acquire while on the back of the sheep will be proportionally greater, other conditions being the same, the greater the number of fibers and the amount of grease; for if the fibers are coarse and sparsely distributed over the skin of the animal, these foreign matters will have less chance to be caught and held by the fleece. The breed of the sheep has also a considerable influence in determining the amount and character of the impurities to be found in the fleece.

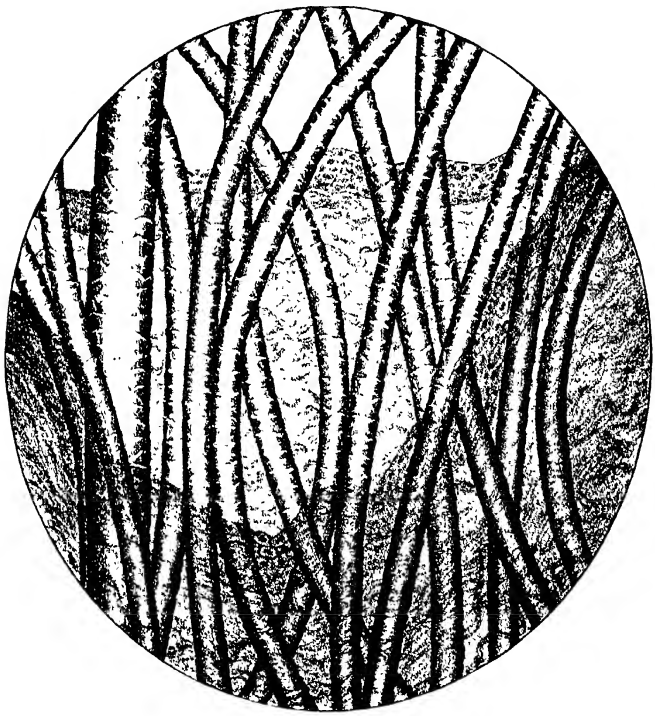

FIG. 3.—Typical Wool Fibers.

Some breeds of sheep secrete a larger amount of greasy matters than others, and in general it may be stated that the more highly the sheep are bred and the greater the proportion of blooded stock in the sheep, the greater will be the amount of grease found in the fleece.

The geographical distribution of the sheep is also a condition influencing both the nature and the amount of the impurities in the wool. The character of the soil and pasturage on which the sheep range has an influence in determining the amount and character of the greasy matters exuded through the glands of the skin, as well as

the nature and amount of the perspiration given off by the sheep. Wool grown in the Western States, where the soil is rather alkaline in character, appears to give less grease than wool from the eastern part of the country. The influence of the soil, climate, pasturage, etc., on the composition and extent of the greasy matters in wool is but indifferently understood, and would be an interesting question for the textile chemist to investigate.

As to the accidental impurities, such as sand, dirt, burrs, etc., these will vary largely with the nature of the country in which the sheep are grown, together with the character of the vegetation, care of the sheep, etc. In sandy soils, of course, a greater percentage of sand will be found in the wool than that from soils of a less sandy nature. Wool from the southwestern part of the United States, which is grown on very sandy soils, is particularly contaminated with this impurity.

Wools from South American countries, where the vegetation is of such a nature that the fleece becomes filled with cockle-burrs, spear-grass, etc., show a much larger amount of such accidental impurities than wool grown in countries free from these wild vegetable growths.[2]

2. Nature of the Impurities in Wool.

It is customary to classify the impurities in raw wool under three general divisions:—

(a) *Natural grease* or *yolk*, consisting of fatty substances insoluble in water, but soluble in volatile solvents and emulsified by alkaline and soapy solutions.

(b) *Dried-up perspiration* or *suint* (so called from the French word for sweat), consisting chiefly of potash salts of various organic acids, soluble in water and easily removed by washing.

(c) *Dirt* and *sand* and *vegetable matter* which are mechanically enclosed in the fleece.[3]

The region round the breast and shoulders of the sheep appears to secrete greasy matters most abundantly, so it is apparent that different portions of the fleece will contain different amounts of yolk; and the same is also true in a general manner of the amount of suint which may be found in various regions of the fleece.

It is not customary in this country to make any distinction between yolk and suint, since in the usual methods of scouring wool in vogue

[2] Many classes of the finest merinos and crossbreds contain a large amount of vegetable impurities in the greasy state; they mix with the fibers and become practically a portion of them. They consist chiefly of burr, but in addition seeds, twigs, leaves, grass, straw, heads of flowers, seed pods, sticks, etc., adhere to the fiber as the sheep pass or rub against them. The practice of tying up fleeces with straw rope, and of having the woolpacks made from loosely-twisted vegetable fibers, also increases the amount of vegetable fiber in wool. The latter has been largely overcome lately by the better tying-up of the fleece, and the use of paper-lined and better packs.

[3] Besides the ordinary natural impurities in wool, there will also frequently occur in the fleece pitchy or tarry matters which have been used for the marking of the sheep for purposes of identification. Pitch is very difficult to remove from the wool by means of soaps and alkalies. It is claimed, however, that by washing the wool in a solution containing about 3 parts of aniline oil per 100 parts of water, the pitch will be removed; after which the wool may be scoured in the usual manner with soap and alkali. Other aromatic bases, such as pyridine and quinoline, may also be employed for the removal of pitch; but as aniline oil is soluble in water to the extent of 3 to 5 percent it is to be preferred. (H. Bunsel, *Ger. Pat.* 97,398 of 1896.)

in the United States both of these substances are removed in one operation. Due to this fact the term "yolk" has become a general one for all these natural impurities of the fleece. Perhaps a better distinction in nomenclature between these substances and one which would lead to less confusion as to their proper meaning, would be "wool-fat" and "wool-perspiration." This distinction is a good one for the scourer to bear in mind, as these two substances are of entirely different origin, possess different properties, and behave in a different manner towards the various materials employed in the scouring of wool. It is only in a few foreign localities, such as Belgium and France, where a previous steeping operation is employed to remove and utilize the soluble compounds of the fleece, that this sharp distinction between yolk and suint is preserved.

3. Wool-fat.

This is a greasy substance of a brownish yellow color, and an odor reminding one of sheep, as would be most natural to expect. Wool-fat differs essentially in its properties from most other animal fats in the following features: The majority of animal fats, such as lard, tallow, etc., consist of compounds of glycerin with the higher fatty acids like stearic, oleic, and palmitic acids, and when these fats are boiled with caustic alkalies a soluble soap is formed, consisting of the alkali salt of the fatty acid, glycerin being also formed in the process. This reaction of a fat or oil with an alkali is known by the name of "saponification," which really means the formation of a soap. Wool-fat, on the other hand, consists in considerable part of an alcohol-like substance known as *cholesterol,* and does not decompose when treated with caustic alkalies into a soap and glycerin, but is what might be termed "unsaponifiable." Ordinary animal fats, as is well known, are not only insoluble in water, but also do not readily form an emulsion with water; that is to say, when a liquid fat is shaken up with water, a good emulsion [4] is not formed, as the mixture of water and fat will soon separate into two distinct layers on standing. In this respect wool-fat differs from the other animal fats in that it very readily forms an emulsion with water which is very permanent. If a small amount of wool-fat be placed in the palm of the hand, for instance, and rubbed with an equal quantity of water, a creamy mixture will soon be formed, which can easily be removed from the hand by washing with water. With warm water and with alkaline solutions, wool-fat forms emulsions with even more readiness than with cold water. This emulsifying property of wool-fat is a very helpful one in the scouring of wool, as it permits of the comparatively easy removal of the grease at low temperatures and with weak alkaline solu-

[4] By an emulsion of an oil or fat with water is meant a mechanical mixture obtained by agitation, whereby the fatty matter is broken up into minute portions which remain evenly disseminated throughout the mass of the liquid in such a manner that the fat does not collect together again and separate from the watery medium There is no actual solution of fatty matter in the water, but a simple division of the fat into small particles which remain suspended in the water. An emulsion usually has a milky appearance; in fact, milk is a good example of an emulsion. A good emulsion is one which remains permanent for a long time and under varying conditions of temperature.

tions. The majority of scourers do not recognize this property to its full significance, and think that it is the alkali which plays the chief rôle in the cleansing of the wool-fiber.

In its chemical composition wool-fat does not appear to be a simple compound, but evidently consists of a mixture of several different ingredients. The exact nature and character of the various constituents of wool-fat have not been thoroughly determined; but it has been found that this substance may be separated into two general portions by a treatment with boiling alcohol. This liquid dissolves a part of the fat and leaves another portion as insoluble. The soluble portion appears to consist in general of free alcohols, together with their compounds with several organic acids, among which may be mentioned formic and acetic acids.[5]

The free alcohols are not cholesterol and its related bodies, but consist of some of the lower alcohols, among which appears to be ceryl alcohol. That portion of the wool-fat insoluble in alcohol is soluble in ether, benzene, and carbon disulfide, and consists of cholesterol and the salts of this body with several of the common organic acids. Some investigators have claimed that these latter acids are chiefly oleic, palmitic, and stearic; but it is likely that these compounds have been derived from the soap solutions employed in scouring the grease from the wool, and are not really constituents of the wool-fat itself; for in wool-fat derived directly from the fleece by solution in naphtha, these bodies have apparently not been found. If any considerable quantities of these fatty acid salts with cholesterol were present in pure wool-fat, this substance would exhibit a greater iodine absorption equivalent, and would also show a different saponification value, because these salts would be rather easily saponified with caustic alkalies, being decomposed into a soluble soap and free cholesterol; as this behavior is not the case, it casts a doubt on the actual occurrence of these bodies in wool-fat.[6]

On account of the low iodine value of both the fatty acids and the alcohols, Lewkowitsch disagrees with the former prevalent idea that neutral wool-fat is a mixture of the salts of cholesterol with oleic and stearic acids. Reasoning both from the low molecular

[5] Buisine (*Dingler's Polytechnische Journal*, Vol 255, p. 88) obtained ceryl cerotate from wool grease by saponifying with alcoholic potash at 100° C., then distilling off the alcohol, forming the barium salt, and treating with boiling alcohol. Lewkowitch, however, disputes this.

[6] The following description of the chemical and physical constants of wool-fat are given by Allen and Lewkowitsch:

Specific gravity (at 15° C.)	0 973
Specific gravity (at 100° C.)	0 901
Solidifying point	30° C.
Melting point	31 to 42° C.
Saponification value	98 to 102
Iodine value	26 to 29%
Alcohols	43 6%
Fatty acids	59.8%

The constants for the mixed fatty acids and alcohols obtained from wool-fat are given as follows:

	Fatty Acids	Alcohols
Solidifying point	40° C.	28° C.
Melting point	41.8° C.	33.5° C.
Mean molecular weight	327 5	239.
Iodine value	17%	36%

weight and the iodine values, he is of the opinion that lower saturated alcohols are present, and that the fatty acids cannot consist to any great extent of oleic acid, but rather consist of hydroxy-acids, as they readily give off the elements of water at temperatures slightly above 100°C., with the consequent formation of inner anhydrides or lactones.[7]

Salts of glycerin with the fatty acids do not appear to be present in wool-fat, and in its purified condition it is free from uncombined acids. Wool-fat, in fact, more resembles beeswax in its chemical nature rather than the ordinary animal fats, and on this account it would, perhaps, be better to designate it as "wool-wax."

4. Degras.

When employed for the greasing or "stuffing" of leathers, wool-grease is generally known under the name of "degras." This term, in the proper sense of the word, should apply only to the product obtained from wool-grease; but, unfortunately, the same term has also been applied to quite a variety of oils and greases employed by tanners without any special distinction between the different origins of the products so designated. The same term also is often taken to include what should more properly be known as "sod-oil." This latter substance is entirely different in its composition and properties from wool-grease, as it is a manufactured greasy substance extracted from leather which has been curried with fish-oils, and contains a resinous substance in its make-up which is not to be found in true "degras" from wool-grease. The confusion in the terms has probably arisen from the fact that in former times the sod-oil was known as degras, whereas, in later times, when wool-grease came to be employed for the same purposes, it was also given the same name; and at the present time the wool-grease has taken to itself completely the name of its former substitute.

As already mentioned, wool-grease has been employed for the greasing of horses' hoofs, but some objection has been raised to its indiscriminate use in this direction, from the fact that a considerable quantity of the wool-grease appearing on the market contains rather a large proportion of free acid,[8] which in time causes a deterioration of the material of the hoof. Properly prepared lanolin or purified wool-grease, however, should not be open to this objection; so when this material is used for the purpose here mentioned, care should be taken to see that it is free from such objectionable matters.

5. Cholesterol.

As already mentioned, this forms one of the distinctive ingredients of wool-fat and it has been isolated and studied with more or less pre-

[7] Darmstaedter and Lifschuetz have claimed to have isolated the following substances from wool-fat: *Lanoceric acid*, apparently having the chemical composition of $C_{30}H_{60}O_4$, insoluble in water, but readily soluble in boiling alcohol. It crystallizes from its solution in the latter on cooling in the form of thin plates having a melting point of 87 to 88° C. *Lanopalmitic acid*, of a melting point of 87 to 88° C., and solidifying at 83 to 85° C. to a lustrous crystalline mass. *Carnaubic* and *myristic* acids were also discovered together with an oily acid resembling oleic acid. A volatile acid, which was probably *caproic acid*, was also isolated. Among the alcohols present *carnaubyl alcohol* was definitely identified.

[8] This results from the use of acid in the precipitation of the wool-grease from the waste scouring liquors, and the subsequent imperfect purification of the grease.

cision by a number of investigators. It is a solid substance, and chemi cally appears to be a monatomic alcohol containing as high as twent six carbon atoms in its molecule. Besides its occurrence in wool-fa it also seems to be an almost universal constituent of many anim tissues, being present in small quantities in several of the juices ar fats in the animal organism. It occurs, for instance, in the human ha and skin, in the feathers of birds, and in tissues of the blood, brain, ar the nervous system.

At the present time cholesterol is prepared on rather a large sca from wool-fat, and is utilized chiefly in the manufacture of pharmace tical salves, for softening leather, for belt dressings, and for the grea ing of horses' hoofs, etc. The salves prepared from it are general known under the name of *lanolin* compounds;[9] and it is of valu for such use on account of the fact that it is a grease which is ve readily and completely absorbed by the tissues of the skin, and if the are suitable medicinal principles incorporated with the grease, the will also be absorbed and thus brought into the system. The peculi healing qualities of wool-grease have long been known, and this sul stance, together with a number of pharmaceutical preparations ma with it as an active constituent, have long appeared in the vari pharmacopeias, both of ancient and modern medicine.[10] In former times it was largely prepared from gall stones, in which cholesterol occurs in rather large amount.

Cholesterol also appears to be present in various vegetable tissues; it has been found, for instance, in the extract from beet-root. Its occurrence has also been proven in various fish oils, and more especially in cod-liver oil. In the animal system it appears to be more or less generally present in all biliary products.

Cholesterol may be prepared in the pure condition from wool-grease by boiling the latter with an alcoholic solution of caustic

[9] As preparations of purified wool-fat (known as *lanolin* compounds) are coming into quite extensive use from the fact that large quantities of wool-grease are now recovered which formerly were allowed to go to waste, it may be of interest at this point to describe the methods employed for the testing of these lanolin preparations. The purity of commercial samples of lanolin may be best ascertained, perhaps, by the application of the following tests:

(a) A small quantity (from 2 to 3 grams) of the lanolin sample is placed in a small flask, after which about 3 c.c. of a 30 percent solution of caustic soda is added, and the mixture heated. Under these conditions, if the sample is pure, no ammonia should be liberated, which fact may be tested by holding a strip of moistened litmus paper at the mouth of the flask so that it may come in contact with the vapors being given off from the heated mixture of grease and alkali. If the red litmus paper retains its color no ammonia is present; but if the test paper turns blue, this will indicate that ammonia is being evolved, and will show that the sample being tested is not of the required purity.

(b) About 10 grams of the lanolin are mixed with about 50 c.c. of distilled water in a glass beaker and then heated on a water-bath. If the lanolin is pure in quality it should form under these conditions a clear oil. If the sample is impure the mixture will become frothy and turbid.

(c) If the sample of lanolin as tested above becomes oily, the oil thus separated should be free from glycerin.

(d) When the sample of lanolin is mixed with a small quantity of water, and the mixture well rubbed together on a glass plate, the resulting mass should be sticky and of the consistency of a paste, and should take up over 100 percent of water. If the sample, however, is impure the mixed product will possess a soap-like smoothness, and will not adhere to a spatula when rubbed.

[10] Wool-fat was used as a recognized pharmaceutical preparation by the early Greeks, as mention has been found of it in the writings of the Greek physician Dioscorides, who lived in the first century of the Christian era. From his description of the substance it was evidently employed in the form of a thick emulsion with water, and the product so obtained was known under the name of *oesypus*, which name it retained for a long time among pharmacists, even down to comparatively recent times.

potash, whereby the greasy matters become saponified to a certain extent, and the free cholesterol is liberated. It is then separated from the other substances present by agitating the saponified mass with ether. This solvent dissolves the cholesterol, but leaves as an insoluble residue the saponified matters, which consist for the most part of soaps. The ethereal layer is then removed and the solvent distilled off, leaving the cholesterol.

Pure cholesterol, as prepared from wool-fat, is insoluble in water, but readily soluble in hot 95 percent alcohol, from which solution it crystallizes in white monoclinic plates containing one molecule of water of crystallization. It is also soluble in ether and fatty acids, and in chloroform. From its solution in the latter solvent it may be crystallized in anhydrous needles.

Though perfectly insoluble in water, cholesterol, nevertheless, mixes with about its own weight of water to form a solid emulsion, which shows no tendency to separate into its respective constituents, even on very prolonged standing and exposure to widely varying temperatures.

Cholesterol is somewhat heavier than water, having a specific gravity of 1.067. When in the pure anhydrous condition, its melting point is 145°C.

The chemical formula of cholesterol has never been ascertained with any degree of exactness, though from analyses of various samples of this substance it has been asserted that there are evidently three homologues of cholesterol varying slightly in their chemical composition from one another, depending on the exact source of the product. These three homologues have been given the following chemical formulas: $C_{25}H_{42}O$, $C_{26}H_{44}O$, and $C_{27}H_{46}O$.[11] The cholesterol corresponding to the last formula was prepared from biliary calculi.

By cautious heating, cholesterol may be volatilized without decomposition, and, furthermore, by proper heating, it may be distilled in a vacuum. The alcoholic solution of cholesterol is neutral in reaction, and it causes a left-handed rotation of the plane of polarized light; the specific rotation (for the sodium spectrum line) being from 36.6 to 31.1, according to different observers. By the addition of a dilute solution of bromine in carbon disulfide to a solution of cholesterol in alcohol, a bromine addition product which may be called cholesterol dibromide may be obtained.[12] It appears to possess the formula

[11] From the investigations of Mauthner and Suida (*Monatshefte*, Vol. 15, page 85) on cholestene, $C_{27}H_{46}$, which is presumably the hydrocarbon from which cholesterol is derived, it may be concluded that these compounds to which cholesterol belongs are capable of taking up only one molecule of a halogen, and that the saturated hydrocarbon from which they are derived may be represented by the formula $C_{27}H_{48}$, and must, therefore, contain closed chains. There also exists in the nuclear portions of the compounds at least one asymmetric carbon atom. Since no halogen acid is eliminated when the compounds are treated with alcoholic potash, the group $-CH=CH-$ is absent, the remarkable stability of the compounds being probably explained by the presence of two directly linked carbon atoms, to each of which two other carbon atoms are immediately attached. The unknown position taken by the halogen atoms in the cholesterol molecule makes it uncertain whether all the closed chains in the compounds are fully saturated.

[12] By passing chlorine into a solution of cholesterol in chloroform cholesterol dichloride is obtained having the formula $C_{27}H_{46}OCl_2 + H_2O$ It becomes anhydrous at 100° C., and melts at 136° C. By warming this cholesterol dichloride with acetic anhydride, a body known as cholesterylic acetate dichloride is obtained, having the formula $C_{27}H_{44}Cl_2.OC_2H_3O$. (Mauthner and Suida, *Monatshefte*, Vol. 15, page 85.)

$C_{26}H_{44}O.Br_2$; it may be isolated in the form of colorless needles having a melting point of 147°C. On treatment with reducing agents, such as stannous chloride in hydrochloric acid solution, it is decomposed into cholesterol and hydrobromic acid. An iodine derivative very similar to the bromine product has also been obtained.[13]

Cholesterol is susceptible to oxidation when treated with a chromic acid mixture prepared from a solution of potassium bichromate in concentrated sulfuric acid; under these circumstances it is converted into a white amorphous powder, which apparently corresponds to oxycholic acid, having the formula $C_{26}H_{40}O_6$. In the same reaction there are also produced small amounts of various acids of the acetic acid series.

Cholesterol behaves in a manner quite different from most other vegetable or animal fats and oils. While the latter compounds are derivatives of glycerin with various fatty acids, cholesterol exhibits the chemical characteristics of an alcohol. A few considerations of the reactions of ordinary animal fats as compared with the corresponding ones of cholesterol will serve to define this difference more clearly; glycerin is a substance possessing an alcoholic nature, and, in consequence, towards acids behaves after the manner of a mild base; that is to say, it is capable of combining with acids to give salts very much after the manner of ordinary alkalies. These salts of glycerin with the acids commonly known as the "fatty acids" make up the principal constituents of the different oils and fats. When these glycerin salts are treated with strong alkalies, which have a considerable affinity for the fatty acids, the former are decomposed into free glycerin and the corresponding salts of the alkali with the fatty acids; the latter bodies being commonly known to us as "soaps." This reaction has been given, in chemical nomenclature, the name of "saponification" or "hydrolysis." When cholesterol, however, is treated in this manner with caustic alkalies, no such saponification takes place; in other words, the cholesterol is spoken of as being "unsaponifiable." This reaction is an important one to bear in mind, owing to the fact that in many minds there is an erroneous impression that in the treatment of the greasy matters on wool with alkalies there is a considerable saponification of the wool-fat so as to form a soluble soap. The only actual saponification which takes place in the scouring of wool with alkalies would be that of a small amount of free fatty acid which at times is to be found in wool grease, and even in this case it is quite doubtful if any actual saponification takes place under the conditions which exist in the scouring process, where the concentration of the alkali is rather low and the temperature is also far below the boiling point; and, furthermore, where the alkali employed is not caustic soda or potash, but only the carbonated alkalies which under the circumstances would form soaps with difficulty.

The alcoholic nature of cholesterol is further evidenced by the fact that when boiled with about 1 to 1½ times its amount of acetic anhy-

[13] The calculated iodine absorption value of cholesterol is 68.3, and this has been closely approximated to in actual determinations.

dride it is converted into an acetate,[14] that is to say, being alcoholic in nature, in the same manner as already mentioned for glycerin, it will combine with acids to yield salts. Owing to the fact that the acetate of cholesterol thus formed shows that for each molecule of acetic acid there is required also one molecule of the cholesterol, we conclude that cholesterol is a monatomic alcohol,[15] that is to say, it has present in its molecule only one group capable of combining with acids to give salts.[16] Glycerin, on the other hand, is what is known as a triatomic alcohol, as it combines with three molecules of acid. The acetate of cholesterol is nearly insoluble in cold alcohol, and only sparingly soluble in hot alcohol.[17] In ether, however, it is readily soluble, and from this solution it may be crystallized in the form of small needles, having a melting point of 92°C. A corresponding salt of cholesterol may also be obtained with benzoic acid, being prepared by heating cholesterol with benzoic anhydride[18] in a sealed tube to a temperature of 200°C. This cholesterol benzoate is also soluble in ether, from which solution it may be crystallized in rectangular plates having a melting point of 150°C.[19] It is only very sparingly soluble even in hot alcohol.[20]

[14] On heating cholesterol with acetic anhydride in a reflux apparatus and cooling, the acetate separates out in the form of flocks; on crystallization from benzene, it forms groups of needles which melt at 113° C., and decompose at a somewhat higher temperature, losing acetic acid; water acts on it in a similar manner. (Rayman, *Bulletin Société chimique,* Vol 47, page 898.)

[15] By heating cholesterol with phosphorus pentachloride cholesteryl chloride may be formed; it is obtained in the form of small scales melting at 96° C. (Rayman, *Bulletin Société chimique*, Vol. 47, page 898.)

[16] Nitro-cholesterol is obtained when a hot saturated solution of cholesterol in glacial acetic acid is treated with concentrated nitric acid. It is a reddish yellow amorphous substance, melting at 93° C. without decomposition, and readily soluble in alcohol, ether, ammonia, and alkalies, but insoluble in water. (Remitzer, *Monatshefte fur Chemie,* Vol. 9, page 421.)

[17] Cholesteryl acetate, $C_{27}H_{45}O.C_2H_8O_2$, appears to exist in three modifications: The first is obtained by crystallizing it from solvents; when the crystals are warmed they become cloudy before melting, owing to the formation of a mass of crystals of the third modification. The second modification is obtained in the form of sphero-crystals when the melted substance is quickly cooled; if xylene is added, the single crystals can be obtained in the form of large thin monosymmetric leaves. The third modification is formed when either of the other two is heated or when the melted substance is slowly cooled. (Reinitzer, *Monatshefte fur Chemie*, Vol. 9, page 421.)

[18] According to Obermuller (*Zeitschrift fur physiologische Chemie,* Vol. 15, page 37), the benzoate of cholesterol may be best prepared by the action of benzoyl chloride on cholesterol, and this preparation may be employed for the quantitative estimation of cholesterol. It has the formula of $C_{27}H_{45}.C_7H_5O_2$ A similar compound may also be prepared from iso-cholesterol. If sodium (or potassium) is placed in an ethereal solution of cholesterol, a compound may be obtained known as sodium (or potassium) cholesteroxide, and having the formula, $C_{27}H_{45}ONa$ (or K). Obermuller also describes cholesteryl phthalate, $C_6H_4(COO\,C_{27}H_{45})_2$, prepared by heating phthalic anhydride and cholesterol at 180° C. Cholesteryl benzyl ether, $C_{27}H_{45}O\,C_7H_7$, is prepared from sodium cholesteroxide with benzyl chloride at 100° C.

[19] Cholesterol benzoate also exists in three modifications. The first is obtained by crystallization from a solvent, the crystals melting at a higher temperature than those of the other two modifications, and remain clear when heated; the second modification is formed when the melted substance is quickly cooled; the third is obtained by cooling the melted substance slowly. Both cholesterol benzoate and acetate show a peculiar color phenomenon when melted and then cooled. (Reinitzer, *Monatshefte fur Chemie,* Vol. 9, page 421). This peculiar property is explained by the assumption that these two bodies may exist in the form of "liquid crystals." They melt sharply at a definite temperature to milky liquids, and these on being further heated suddenly become clear, also at a definite temperature. There are a few other substances known to possess this same property in addition to the cholesterol esters. The idea of the milky liquids being "liquid crystals" was deduced from the fact that the turbid liquids obtained not only possessed the usual properties of liquids, but also possessed properties which had hitherto been observed only in the case of crystalline substances; that is, the property of double refraction and of giving interference colors when examined in polarized light.

[20] Other esters of cholesterol may be prepared in a similar manner. On boiling any of these esters with alcoholic potash they are readily saponified with the liberation of free cholesterol.

6. Iso-Cholesterol.

In addition to cholesterol there also occurs in wool-fat a substance of practically the same apparent composition to which has been given the name of *iso-cholesterol.* It is probably a chemically isomeric body, as it has the same approximate formula as cholesterol, and resembles the latter body in many of its properties and reactions. It is readily soluble in hot but only sparingly so in cold alcohol, so that on cooling its hot alcoholic solution it separates out in a jelly-like mass. The solution of iso-cholesterol, however, differs from that of cholesterol in that it rotates the plane of polarized light to the right instead of to the left; its solution in ether having the specific rotation of 60° to the right.

In its chemical reactions, iso-cholesterol is very analogous to cholesterol itself, as it forms salts with acids in the same manner, and both the acetate and benzoate have been prepared. The acetate is an isomorphous substance, but the benzoate can be obtained in fine crystalline needles having a melting point of 190°C. The separation of iso-cholesterol from cholesterol is brought about, in fact, by the preparation of the benzoic acid salts. The mixture of the two bodies is heated for about thirty hours in a sealed tube at 200°C. with four times its weight of benzoic acid or benzoic anhydride The product obtained by this treatment consists of the benzoates of the two cholesterols, together with the excess of benzoic acid. The mass is extracted several times with boiling alcohol, which dissolves out the unchanged benzoic acid and leaves the benzoates as an insoluble residue. The latter is then dissolved in ether, and the solution is allowed to crystallize by evaporation.

The cholesterol benzoate separates out in the form of shining rectangular plates, while the iso-cholesterol benzoate subsequently separates out in the form of a light crystalline powder, and in this manner the two substances may be rather readily separated from one another.

In order to obtain the free cholesterols themselves, the separate salts are boiled with an alcoholic solution of caustic potash, which decomposes the salts, so that on dilution of the solution with water the free cholesterol separates out.

A rather remarkable fact observed in connection with cholesterol and iso-cholesterol is that though both of these bodies melt at about the same temperature, yet a mixture of the two has a lower melting point than either one of them separately.

7. Tests for Cholesterol.

As cholesterol is a common ingredient of all wool-fat compounds, it is of considerable interest to know of some definite tests whereby this body may be identified and recognized. With this object in view, the following chemical tests are given as being characteristic of cholesterol.

(a) If a small sample of cholesterol be dissolved in chloroform, and the solution treated with an equal volume of strong sulfuric acid, the liquid will exhibit quite an interesting color phenomenon, becoming first bluish red, then changing to violet, then to green, and finally to yellow. This test is a very characteristic one, and is known as *Salkowski's reaction.*

(b) Another test known as the *Liebermann-Burchard reaction* is the following: The chloroform solution of the cholesterol is treated with a few drops of acetic anhydride, and then concentrated sulfuric acid is added drop by drop; the color of the liquid will at first become red, then change to blue, and finally become green.

(c) A third test for cholesterol, which, however, is not so simple or so pronounced as the two above given, is the following. When a small quantity of cholesterol is cautiously heated with a drop of concentrated nitric acid on the lid of a porcelain crucible, a yellow stain is produced; on the addition of a small amount of ammonia water to this a yellowish red color is obtained. Furthermore, if a small quantity of cholesterol be placed on the lid of a porcelain crucible and treated with a drop of a mixture consisting of three parts of concentrated hydrochloric acid and one part of a ten percent solution of ferric chloride, and the mixture thus obtained be evaporated to dryness, a residue is obtained having a violet red color which rapidly changes to blue.[21]

Iso-cholesterol gives the same reaction as cholesterol itself with the nitric acid and ammonia test, but it gives no reaction with Salkowski's test. With the Liebermann Burchard test a yellow color is produced which changes to reddish yellow and at the same time exhibits a greenish fluorescence.

8. Wool-oil.

Besides the greasy matter which is to be found on the external portion of the wool fiber, and commonly known as wool-fat, there is another kind of fat also present in the fiber, which, however, is of different origin from that of the ordinary wool-fat; it also occurs in a different portion of the fiber, and performs a different function in the animal economy. The fatty matter here referred to had best be known under the name of *wool-oil,* and occurs in the internal structure of the fiber itself, no doubt within or between the cortical and medullary cells.

Whereas the ordinary wool-fat is secreted by special sebaceous glands in the skin located around but entirely separate and distinct from the glands from which the fiber proper takes its growth, this wool-oil appears to be a secretion of the hair follicle itself, and therefore forms an intrinsic part of the organic structure of the fiber.

While the function of the wool-fat as an external coating on the fiber appears to be solely that of a protective agent to prevent mechanical injury and felting of the fiber during its growth, the function of the wool-oil seems to be that of affording a proper internal lubrication within the cellular structure of the fiber, thus giving it the qualities of suppleness and high elasticity. If it were not for the presence of this oil within and between the cells the fiber would be brittle and inelastic, and it would also be harsh and lifeless, and without the characteristic resilience which is such an important quality of

[21] According to Obermuller (*Chemische Centralblatt*, 1890, p 299), the formation of cholesterol propionate is the most characteristic and delicate test for cholesterol, as the colors which this substance assumes during cooling are intense and distinct, and are also of longer duration than many of the other cholesterol reactions The test is carried out as follows: 10 grams of cholesterol are melted with 5 grams of propionic anhydride. The propionate, $C_2H_5COO.C_{27}H_{45}$, crystallizes in rhombic plates, and as the substance cools it gradually assumes the colors violet, blue, green, dark-green, orange, carmine, and finally copper-red.

the wool fiber, and which makes it so valuable as a spinning and clothing material.

The removal of the wool-fat which is necessary for the purpose of manufacturing and dyeing wool does not appreciably affect the physical qualities of the fiber proper and hence the wool-fat cannot be considered in any sense as an integral part of the fiber, but, on the other hand, if the wool-oil is removed, the fiber becomes worthless for the purposes for which it is intended, and its physical properties suffer a great deterioration.

The amount of wool-oil actually present in the wool fiber is rather difficult to estimate with any degree of accuracy, as it is hard to effect a satisfactory separation of it from the wool-fat for purposes of analysis. Its amount, however, has been variously estimated at from one to two percent on the weight of the fiber; for it has been found that this amount of oil is left in wool after it has been properly scoured, and if less than this amount is left, the physical properties of the fiber will suffer considerably. The nature of this oil, either with respect to its physical or chemical characteristics, has never been investigated in any but a casual manner, though from the importance of the oil in the fiber as affecting its good qualities, such an investigation of its properties would necessarily be of considerable value.[22]

From the remarks which have already been made concerning the part which this wool-oil plays in the structure and properties of the fiber, it will be readily understood that the scouring of wool, in whatever form and by whatever means, should not be overdone; that is, should not be carried to such an extent that not only the wool-fat is completely removed, but also the wool-oil within the fiber, as this would cause the latter to become harsh and lifeless.

When the scouring is carried out by means of soap and alkalies, and at moderate temperatures, there does not appear to be much danger of carrying the scouring too far, and as a result remove the wool-oil unintentionally. This oil is apparently very readily soluble in such solvents as naphtha; probably even more so than the external wool-fat itself, and hence the importance of the proper regulation of the solvent or naphtha process so as to obtain the desired degree of the removal of the fatty matters. Well-scoured wool should not have less than one percent of oil remaining in it, nor more than two percent.

9. Suint or Wool Perspiration.

It has been pointed out in a former paragraph that the wool fiber during its growth in the fleece becomes saturated with a considerable amount of the perspiration from the sheep's skin, and that through the natural evaporation of this substance there was left in and on the fiber

[22] Some observers have contended that any good evidence for the existence of a separate wool-oil are entirely lacking, and the claim is made that the lubrication of the fiber is brought about by a small amount of the ordinary wool-grease which interpenetrates the elements of the fiber, and that the oily matter which is left within the fiber under proper conditions of scouring is simply this absorbed wool grease, and there is no reason for assuming the existence of a special and different character of oil. The present author himself is somewhat sceptical as to the existence and identity of this so called wool-oil. The subject needs careful scientific investigation before the facts can be definitely ascertained.

quite a large amount of various potash salts or other mineral or solid matters originally present in the perspiration. This dried-up residue of wool perspiration is soluble in water, and, as before stated, consists principally of compounds of potash with various organic acids.

The chief acids which have so far been identified in suint are oleic, stearic, hyenic and acetic acids; small amounts of chlorides, phosphates and sulfates are also present, together with minute quantities of various metals. The residue left after the ignition of suint has been analyzed with the following result:—

	Percent
Potassium carbonate	86.78
Potassium sulfate	6.18
Potassium chloride	2.83
Phosphorus, silica, lime, etc	4.21

It must not be thought, however, that because the ignited residue or ash of suint contains a large proportion of potassium carbonate, that this substance existed in that form in the suint itself. The potassium carbonate is derived from the ignition of the various fatty-acid salts of the original suint, and it is doubtful if any carbonate at all exists in that substance. This point is brought out because there are some who think that because potassium carbonate can be obtained from the ash of suint, the same substance must have originally been present in the wool, and consequently it has been stated on account of such erroneous ideas that the previous removal of the suint, or water-soluble constituents of the impurities on the wool fiber, is not proper, for as it contains such a high proportion of potash (i.e., potassium carbonate), the suint would assist very materially in the scouring of the fiber by reason of the alkali present. This statement is not only erroneous and misleading, but is also vicious; for far from being beneficial in the scouring operation, the potash salts actually present in the wool-suint are to a certain extent deleterious by reason of the fact that they introduce various metallic salts into the soap solution, causing a more or less hardening of the water, and a consequent neutralization of some of the scouring power of the soap.

Since dried suint contains about 40 percent of mineral constituents, and as the majority of these consist of potash salts, it may be seen that the wash waters from wool might be utilized as a source of potassium compounds, and more especially potassium carbonate, and these possess a rather high commercial value.

In this country the wash waters from wool are not worked up for their potash salts,[23] and, in fact, where the soap process is employed for scouring the wool is not subjected to a separate washing operation, whereby the potash salts are removed independently of the greasy matters and dirt also on the fiber. The discussion as to the recovery of the suint and the utilization of the potash salts will be taken up in a

[23] During the recent war when potash salts became very scarce in this country and consequently brought a high price, wool scouring establishments in many cases installed plants for the recovery of the waste potash compounds, and this source supplied quite a good deal of potash for the needs of the country.

further section relating to the recovery of the by-products in wool scouring.

The following analyses of samples of different kinds of raw wool by Marckt and Schultz exhibit the relative proportions of the various constituents present in the wool as it comes from the back of the sheep:—

	Sample 1 Percent	Sample 2 Percent	Sample 3 Percent
Water	23.48	12.28	13.28
Wool-fat	7.70	14.66	34.19
Suint	21.48	22.48	10.65
Lime soaps	1.74	6.21	1.39
Dirt	2.03	23.64	8.38
Wool fiber	43 20	20.64	32.11

10. Lime Soaps in Wool.

The lime soaps that are found to be present in raw wool are doubtless derived from the combination between the lime in the dirt and dust coming into the fleece, and the fatty acids that are present to slight extent in the greasy matters of the fiber.

As a rule, the amount of these lime soaps will depend directly on the amount of dirt in the fiber, and those wools containing a large amount of dust and dirt will show a correspondingly large amount of lime soaps. Also, wools grown on soils where a good deal of lime is present will naturally have a larger content of lime soaps than those wools grown on soils of another character.

It is not likely that the lime soaps form a constituent part of the fiber itself, but are confined to the external impurities coating the fiber proper. There is, it is true, a small amount of lime to be found in the ash of the wool fiber which has been cleansed of all foreign matter, but this is only a very small proportion of that which is present in the form of lime soaps.

These lime soaps on the wool fiber are usually overlooked by the scourer in a consideration of the foreign matter present; though they at times may have quite an important influence on the scouring, especially when scouring by means of the solvent naphtha process, whereby the greasy matters are extracted by being dissolved in naphtha.

The lime soaps are of a sticky, insoluble nature, and are rather difficult to satisfactorily remove at the best. They do not dissolve in naphtha, and form greasy precipitates when present in any large amount in this method of scouring. They are removed by being emulsified with soap and alkali solutions, and probably it is the alkaline carbonate present in the scouring bath (the soda ash or the potash, as the case may be), which best effects their removal.

When any very large amount of lime soap is present in the fiber, probably the best method of treatment would be to pass the wool first through an acid bath in order to decompose the lime soap into the free fatty acid and the salt of lime corresponding to the acid used. Hydrochloric acid perhaps is the best to use for this purpose, as the calcium chloride formed is very soluble in water and may be easily removed by washing. Care should be had, however, not to use too

much acid, as otherwise the wool will combine with some of the acid in such a manner that it cannot be well washed out, and as a result, when the wool is afterwards introduced into the soap scouring bath, some of the soap may be precipitated.

Perhaps the safest method is to pass the wool through a weak alkali bath after treatment with the acid and before entering the soap solution. If there is considerable alkali present in the scouring bath, however, there will be but little danger of any soap being precipitated by the acid, as the latter will be neutralized almost immediately by the carbonated alkali. Of course, this treatment with acid before scouring is only to be recommended in the case of wools which contain an unusually large amount of lime soaps.

11. Water Soluble Constituents of Suint.

The suint of wool is a very complex compound as is shown by an examination of its water soluble constituents in which the following substances have been found:—[24]

(1) Free carbonic acid, probably derived from compounds formed by the action of the carbon dioxide of the atmosphere on substances in the suint.

(2) Ammonium carbonate, no doubt formed through the fermentation and decomposition of nitrogenous matter in the suint. The latter substance, like urine, probably contains some urea, and this body readily decomposes into ammonium carbonate.[25]

(3) Potassium carbonate, though whether this salt exists as such in the perspiration as exuded by the sheep has not been determined, it occurs in only small amounts, and may be formed through the interaction of ammonium carbonate on potash salts of the suint.

(4) Various volatile fatty acids, including acetic, propionic, butyric, valeric and capronic acids. These do not occur in the suint in the form of the free acids themselves, but as the potassium salts of these acids. Indications also point to the presence of capric acid.

(5) Higher fatty acids, including œnanthic, caprinic, oleic, stearic and cerotinic acids. These are also present in the form of potassium salts.

(6) Fatty matters of uncertain composition and existing in the state of an emulsion. These matters are probably an emulsion of some of the free cholesterol of the wool-fat with water.

(7) Phenol, existing in the form of potassium sulfonate of phenol. The occurrence of this substance is rather remarkable, and it is more probably an accidental impurity than a naturally occurring substance in wool-perspiration itself.

(8) Lactic acid, which also probably exists in the form of its potassium salt. Glycollic acid is also claimed to have been found.

(9) Benzoic acid; this also occurs in the perspiration of other animals. It is probably derived from the oxidation of aromatic phenolic bodies.

(10) Oxalic acid, which is a common form of the decomposition product of organic tissues.

(11) Succinic acid and malic acid in the form of potassium salts; probably pyrotartaric acid is also present.

(12) Uric acid is generally to be found in all sudorific excretions. Hippuric acid is also present.

[24] Buisine, *Comptes rendus*, Vol. 103, p. 66.

[25] According to Buisine (*Comptes rendus*, Vol. 104, p. 1292), a fresh aqueous solution of wool-suint contains very little ammonia, but after standing for some time the proportion of this alkali increases considerably It apparently results from the decomposition of urea, and exists in the form of carbonate and is completely expelled by boiling. In addition to ammonia, the vapor given off when the solution of suint is boiled contains monomethylamine and trimethylamine, the proportion between the three alkalies being ammonia 95, monomethylamine 4, and trimethylamine 1.

(13) Various amido-acids, including glycocoll, leucine and tyrosine; probably derived from decomposition products of the skin-tissue or of the hair itself.

(14) A coloring matter, apparently quite similar to that occurring in the urine.

The suint in an Australian wool in 100 parts of dry residue gave 7.1 parts of acetic acid, 4 parts of propionic acid, 2.6 parts benzoic acid, 2.5 parts of lactic acid, and 1 part of caprinic acid.

From 1,000 pounds of an average raw wool there may be obtained by extraction with warm water sufficient suint to yield a residue, after evaporation of the steeping liquors, of about 140 to 180 pounds. On the ignition of this residue there may be obtained as much as 70 to 90 pounds of potassium carbonate, and about 5 to 6 pounds of the mixed sulfate and chloride of potassium. It may be said, as a general statement, that the amount of potash salts to be derived from raw unwashed wool will be about 10 percent of the weight of the wool.

12. Natural Coloring Matters.

The great majority of sheep's wool is nearly always white in color, although it may occur in various natural colors, running all the way from light brown up to gray or even black. Even the so-called "white" wool, however, has a small amount of pigment matter in it, which gives it a slight yellowish brown tint which it is the object of bleaching to remove. The natural coloring matter of wool appears to be somewhat differently distributed through the fiber than is the case with artificially applied dyestuffs.

When occurring in the natural condition, the pigment matter seems to be contained particularly in the cells of the cortical layer and in those of the marrow or medulla in a granular form, and to occur to a greater extent in the medullary than in the cortical cells. In fibers which have but a small amount of coloring matter present usually show the cell-wall as practically colorless, and the pigment matter exists as a solid substance sharply differentiated from the substance of the cell itself. In fibers, however, which are strongly colored, the walls of the cells themselves also appear to be impregnated with the coloring matter. In wool which has been artificially dyed, however, the cell-walls are nearly always uniformly colored, and as a consequence the medullary cells or marrow become less pronounced in their outline and cannot sometimes be distinguished from the cortical cells; but with naturally colored wools the medullary cells are usually rendered more distinct and prominent in their outline by reason of the deposit of pigment matter within the cells.

The composition and properties of the natural coloring matter of wool has received but little attention from chemists, and little definite information can be stated concerning it. It does not, however, appear to be a very permanent color, as it does not withstand the action of most chemical agents as well as the majority of the artificial dyestuffs; it does appear to possess, however, a fair degree of fastness to the action of dilute acid and alkalies, but towards light it is not especially permanent. Whether this pigment matter is a simple chemical substance or a complex mixture of several distinct bodies is not known.

Chapter III.

Scouring of Wool.

1. The General Theory of Wool Scouring.

Wool has been employed as a textile fiber from very early times, and therefore the proper methods of cleansing it from its adhering impurities would naturally be a subject of much consideration, for it is practically impossible to work up the fleece of the sheep through the various manufacturing operations leading to the production of a woven fabric without first cleansing the fiber to a greater or less degree.[1]

In some instances wool is washed in the fleece while still growing upon the sheep. When this is done, simply running water is employed, the sheep being driven into small streams and washed more or less thoroughly. This treatment results in the removal of most of the miscellaneous dust and dirt imbedded in the fleece, though there is also a considerable removal of the soluble salts of the suint, and a certain amount of the wool-grease is also emulsified and carried off. These *washed fleeces,* however, still have considerable grease and other impurities left in the fiber and have to undergo a preliminary scouring as well as unwashed fleeces.

2. Steeping of Wool.

A distinction is to be made between "washed" wool and "scoured" wool: the former indicates wool that has been washed on the back of the sheep before shearing, whereas the latter is used to designate wool that is washed free from impurities after shearing. In washed wool a large proportion of the soluble suint containing most of the inorganic matter and potash salts is removed together with a small amount of the wool-grease which comes off in the form of an emulsion. Such wool, of course, is still in a rather greasy condition when it comes into trade and has to be scoured like ordinary raw wool. The wool is washed in the fleece in order to lessen the weight of impurities and thus save freight; it also gives a better looking and more salable product. The washing is usually carried out with warm water and it is not practical to conduct the process in a very thorough manner.

[1] Before the raw wool is scoured (or even washed if it is to be previously steeped) it is usually opened up and freed as far as possible from sand, dirt and similar foreign bodies by being passed through a machine called a "wolf." This consists essentially of rapidly rotating rollers provided with heavy iron teeth and also with a strong blower fan or air suction to take away the dirt.

The scouring of wool in European establishments is usually conducted somewhat differently than it is here in America, as it is customary to employ a steeping or washing process previous to the scouring with soap and alkalies. This permits of the removal of most of the soluble suint and a great deal of the miscellaneous dirt. In this washing lukewarm water (140°F.) is used and the operation is so conducted that the raw dirty wool is first washed in water that has been already used for a previous lot and then washed again in a fresh water. In this progressive method of steeping about four different baths are used, so that the last dirty water is fully charged with dissolved suint, and this may be used subsequently for the recovery of the potash salts. There is always a certain amount of grease removed in an emulsion form at the same time, and this contaminates the salts. Apparatus so constructed as to automatically wash the wool in this manner is quite extensively used in Europe.[2] The apparatus consists essentially of a series of tanks and is provided with squeeze rolls at the end of each tank. The raw wool is entered in the first tank and is carried progressively forward through warm water by moving rakes, passes through the squeeze rolls and into the second tank, and so on. Fresh warm water is introduced in the last tank and flows forward to the first tank in a direction opposite to that of the wool, becoming thus more and more charged with the wool suint and finally runs off in a saturated condition from the first tank.

Another process, though using first cold and then warm water, is that of Malard.[3] A further process with suitable apparatus is that of Schuman.[4]

In America the preliminary steeping or washing process is seldom used, but the raw dirty wool is placed directly in the soap scouring bath. The advantage of the European process, of course, lies in the fact that it is comparatively easy to recover the potash salts from the concentrated steeping liquors, and also that the wool entering the soap bath is fairly clean and therefore the scouring liquor does not so soon become too impure for use owing to the suint and dirt coming off with the grease. In this way the valuable soap is more efficiently used in scouring as the soap baths can be used on a greater amount of wool. The American system, on the other hand, has less processing of the wool, less installation and less labor.

To recover the potash from wool steeping liquors these are evaporated to dryness either by boiling down in open pans, or better in vacuum evaporators. The pasty mass so obtained is then dried and calcined in a suitable oven. This usually gives rise to badly smelling gases.[5] The yield of the raw potash salts varies greatly, depending on the character of the wool, but is usually about 6 to 8 percent on the

[2] See Bernhardt, *Ger. Pats.* 175,421; 177,520; and 179,401; and *Fr. Pat.* 345,718. Also see *Jahres Berichte*, 1906, p 381; 1907, p 386; and 1908, p. 348; also *Zeit. Farb. Ind.*, 1905, p. 18.

[3] *Ger. Pats.* 218,522 and 230,299; also *Färb. Zeit.*, 1907, p. 2 and *Elsäss. Textil. Blatt*, 1911, p. 435.

[4] *Ger. Pats.* 225,669 and 229,710; also *Chemiker Zeit Rep.*, 1910, p. 528, and 1911, p. 80.

[5] For the disposition of which see Zahn. *Ger. Pat.* 206,747; also *Jahres Bericht.*, 1909, p. 383.

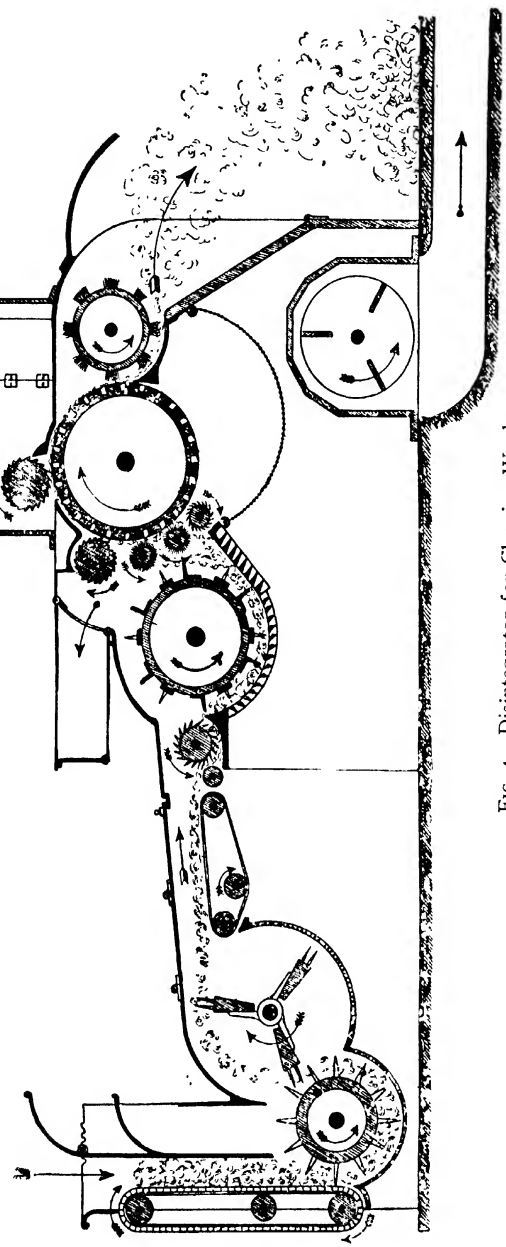

Fig. 4—Disintegrator for Cleaning Wool.

weight of the raw wool. A typical analysis of the raw potash salt is as follows:

	Percent
Potassium carbonate	78.5
" chloride	5.7
" sulfate	2.8
Sodium sulfate	4.6
Insoluble matter	5.0
Organic matter	3.0

A large number of processes have been patented for the utilization of wool steeping liquors, such as for the preparation of ammonia, potassium cyanide, potassium ferrocyanide, fatty acids, etc.

3. Action of Alkaline Liquids.

The use of alkaline liquids for the purpose of removing the greasy materials from wool has apparently been of long practice. Infusions of the barks of certain trees which are capable of yielding a liquid possessing saponaceous qualities were probably among the earliest forms of soapy liquors used for scouring. Stale urine, known under the name of *lant,* was also largely used for this purpose at one time. In fact, lant has been used up to rather recent years as a scouring agent, and no doubt there are isolated instances of its use even at the present time. The offensive nature of lant, however, militates greatly against its use in modern mills, as it generally leaves the wool with a disagreeable odor and a yellowish discoloration.

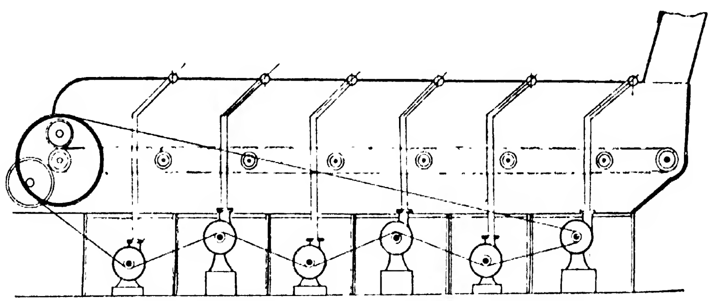

Fig. 5.—Malard's Continuous Desuinting Machine.

In the scouring of wool we must bear in mind the fact that the impurities are present in several forms. The fatty, insoluble matter forms a protective layer on the surface of the fiber, which enables it to resist to a considerable degree the action of water; consequently, when wool is steeped in cold water, only a very small amount of the impurities are removed, with the exception of the loosely-adhering earthy matters, such as dirt, dust, etc., which are mechanically detached from the surface of the fiber by the action of the water. On steeping in hot water, however, especially if accompanied with suitable agita-

tion of the fiber in the liquid, almost all of the soluble matters (such as the potash salts, etc.) pass into solution, while at the same time a considerable portion of the wool-grease is emulsified. A small amount of the dirt and the soluble potash salts is still left enclosed in the fatty matters which remain in the wool. If the fiber, which is thus partially cleansed, is treated with a solution of alkali or soap, the greasy matters become completely emulsified, and are thus removed by the accompanying action of the water present. A previously pointed out,[6] wool-fat is not readily saponified, and even when comparatively strong solutions of alkaline carbonates are employed, it is doubtful if any considerable amount of the fat is actually saponified and removed in the form of a soluble soap. It has been noticed, however, that wool-fat easily forms a stable emulsion with water, and in the presence of alkaline substances or soap the emulsification is greatly accelerated. Therefore, we must regard this method of wool scouring as an emulsion process, the greasy matters being held in suspension in the alkaline liquid, and not dissolved to any extent.[7]

It may be said, in general, that soap solutions are by far the most efficient scouring agents in connection with the proper cleansing of wool, as these solutions have little or no action on the good qualities of the fiber which it is the object of the scourer to retain as far as possible, while at the same time such solutions remove the greasy matters and dirt more effectively than any other agent. Solutions of the carbonated alkalies (soda ash and potash), which are also extensively employed for the scouring of wool in conjunction with solutions of soap, always exert a more or less deleterious action on the strength, elasticity and luster of the wool fiber, nor do such solutions remove the grea e and dirt with as much readiness and thoroughness as do solutions of soap.[8] Solutions of the caustic alkalies are also capable of emulsifying and removing greasy matters, but as their action on the wool fiber itself is a very bad one, they can scarcely be legitimately considered as scouring agents for this class of work; nor, in fact, is their cleansing action as thorough as that of soap solutions.

[6] See page 15.

[7] A peculiar method suggested for the scouring of wool without the use of alkalies or soaps is the following: The material to be scoured is mixed with a quantity of dry, pulverized infusorial earth (kieselguhr), and is then heated to a temperature about 10° to 12° above that of the melting point of the greasy materials in the wool. By constant agitation of this mixture it is claimed that the fat is melted and absorbed by the infusorial earth, which is of an exceedingly porous and absorbent nature (August Eberz, *Ger. Pat.* No. 32,884 of 1884).

During the past few years a similar method of wool scouring has been worked out in the United States, the raw greasy wool being agitated with finely pulverized gypsum. This material being very absorbent, takes up all the grease, dirt and other impurities and is said to leave the wool in a perfectly clean and uninjured condition. It is understood that this process is now being carried out on a large scale with much success in this country. The wool fiber is said to be left in a much better condition than when scoured by the usual processes, as it is not subjected to alkaline liquors and hot solutions of soaps. It is also easy to recover the grease and other by-products from the gypsum used in the process. The details of the process are described in *U. S. Patent* 1,323,641 to the United States Wool Co.

For the degreasing of wool by the use of infusorial earth also see A. Born, *Ger. Pats.* 143,567, 149,825 and 151,238 (see also *Jahres Bericht.*, 1904, p. 385). By the use of a suitable machine the wool is very intimately mixed with finely powdered infusorial earth. This is said to absorb all the suint and grease The material is then run through a "wolf" provided with a strong air-blast and exhauster so that all the earthy matter is dusted from the wool, leaving a pure clean fiber.

[8] *Jour. Soc. Chem. Ind.*, 1905, p. 659.

4. Action of Soaps.

According to Berzelius[9] the usefulness of soaps in scouring depends upon the facility with which neutral soaps decompose on solution in water into "acid soaps" and free alkali.[10] In this connection it may be explained that by a "neutral soap" is meant one in which all of the fatty acid present is exactly neutralized or combined with the alkali from which the soap is made. In order for a neutral soap to be partially resolved into an acid soap and free alkali when dissolved in water, it would be necessary that one or more of the molecules of the

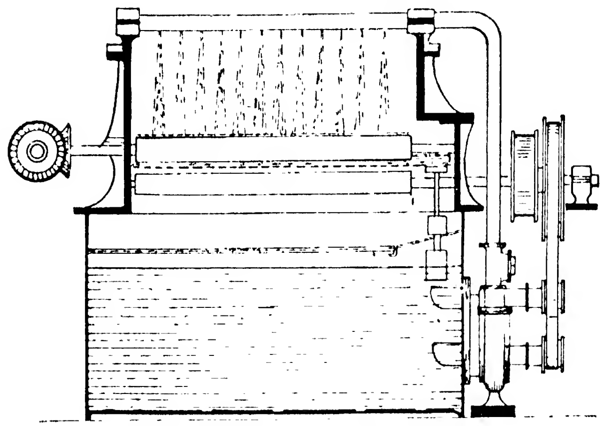

FIG. 6—Cross-section of Malard's Machine.

base (the alkali, which may be either soda, Na_2O, or potash, K_2O, depending upon the nature of the soap) be split off from its combination with the fatty acid, and be replaced by a hydroxyl group supplied by the water present; at the same time, the remaining hydrogen atom of the water would combine with the alkaline base to form free caustic alkali.

[9] *Chem Rev*, Vol 14, p 228

[10] If a neutral soap, carefully prepared and purified so as not to contain any free alkali or uncombined fatty acid, is dissolved in a little hot water to a clear solution, and a considerable quantity of cold distilled water is added, there is produced a marked turbidity due to the formation of an insoluble acid soap, while some caustic soda simultaneously goes into solution. Only a small part of the soap dissolved is affected by this change, which is frequently described as the "hydrolysis" of soap As a rough estimate, and dealing with the average strength of soap solutions used for washing purposes, the amount of alkali liberated in this way would not be more than from two to five grains of caustic soda ($NaOH$) per gallon, a quantity which, under ordinary circumstances, would speedily be converted into sodium carbonate by carbonic acid present in the water An experiment to show this formation of traces of alkali may be made as follows: To a small volume of warm and fairly strong soap solution add a drop or two of phenolphthalein, with which any ordinary soap will give a red color, and then add very dilute sulfuric acid until the red color is just discharged If the solution is now diluted with a considerable volume of distilled water free from any acid, the red color will be restored to some extent, showing the presence of alkali liberated by dilution A more certain way of showing this is to dissolve some soap in alcohol, to filter the solution, and to add to the filtrate a drop or two of phenolphthalein If a red color is produced, add acid until it is just discharged; but if no color is seen, add weak caustic alkali until a very faint pink tinge is seen. On now diluting with water, the liberated alkali will give a full red color with the indicator The extent of hydrolysis varies with different soaps, with the temperature, and with the amount of water added.

As the fatty acids and the bases from which soaps are made are both monovalent in character, it is difficult to understand just how such a decomposition of the soap with water could take place. If the base were of a polyvalent character it would easily be possible to have an acid soap formed by double decomposition with water, or if the acid were of a polyvalent character it would be possible to have a basic soap formed in the same manner. The only manner in which this idea of the formation of an "acid soap" may be represented is to consider that some of the molecules of soap are decomposed into free fatty acid and free caustic alkali by the action of the water, while the remaining molecules of the soap are not so decomposed:—

$$\underbrace{\text{Fatty Acid Radical: NaO}}_{\text{soap}} + \underbrace{\text{H.OH}}_{\text{water}} = \underbrace{\text{Fatty Acid Radical: OH}}_{\text{free fatty acid}} + \underbrace{\text{Na.OH}}_{\text{free caustic alkali.}}$$

Such a conception would be in entire accord with the theory of chemical dissociation of dissolved salts (for a soap may be considered as a salt of sodium with a fatty acid), but the same condition could be realized by taking a solution containing the same relative amounts of soap and caustic alkali, and from practical experience it has been found that such solutions do not act in the same manner as solutions of soap.

An accurate determination of the amount of alkali liberated when soap is dissolved in water is difficult, but the following table gives determinations made with specially prepared neutral soaps, dissolved in the proportion of 1 part of soap to 400 parts of water, the amount of alkali set free being given as percentage of the total alkali originally combined in the soap:

Soaps	Temperature 59° F.	104° F.	192° F.
Cocoanut oil	5.8	1.6	8.5
Cottonseed oil	6.2	8.1	10.4
Palm oil	7.4	7.3	9.6
Beef tallow	6.8	8.5	10.2
Sodium oleate	7.1	5.7	4.1

Too much importance must not be attached to these figures, as different results may be obtained by varying the conditions of the experiment; but as a general rule, soaps made from glycerin compounds of the fatty acids having high molecular weight are more readily hydrolysed than those from fats containing acids of lower molecular weight. Sodium oleate differs in being more hydrolysed in cold than in hot solutions.

Neutral soaps dissolve in strong alcohol without apparent change, and the presence of glycerin somewhat lessens the degree of hydrolysis. There is little or no difference between potash and soda soaps in their behavior with water in this respect.[11]

[11] The recognition of the fact that soaps do undergo a change when dissolved in water has led to the suggestion that their efficiency as detergents may be considered to be partly due to the action of the liberated alkali on the grease which accompanies most dirt. In

Persoz assumes that "neutral soaps" are soluble in hot water without decomposition, but in cold water they are resolved into "acid" and "basic" soaps, and that the latter remove or dissolve the fatty matters by a process of saponification. But in this connection it may be said, apart from the loose use of the terms "acid soap" and "basic soap," that a basic soap would in all probability have far less power of saponification than free caustic alkali itself, as the alkaline or basic character of the caustic alkali has already been partially satisfied by combination with fatty acid; and, furthermore, at the low concentration and temperature at which the scouring solution is employed, even caustic alkali itself would effect very little saponification of a fat, and it would be expected that the "basic" soap would have still less action.

Rotondi, in order to explain why hot soap solutions are more effective than cold ones, claims that neutral soaps on solution are decomposed into "basic" and "acid" soaps, the latter being insoluble in cold and only slightly soluble in hot water. The "basic" soaps, on the other hand, are completely soluble in hot and cold water, and their solutions, on heating, dissolve "acid" soaps, and furthermore, they emulsify fatty matters readily, though no actual saponification of the latter takes place. "Neutral" soaps, however, possess this property only to a slight extent, and "acid" soaps not at all.

These complicated chemical explanations endeavoring to account for the cleansing action of soap solutions appears to the author to be without either satisfactory theoretical or experimental foundation. All of these explanations tend to the point of view that such cleansing action is due to an alkalinity (causticity) in the solution arising either from the formation of free caustic alkali itself or from the formation

dealing with alkalies, it has been pointed out that the amount of saponification of grease produced by weak alkaline solutions in the conditions in which they are used is very slight, and that their effects are to be attributed rather to their powers of emulsifying fats and oils.

As the property which soap also possesses of making emulsions with grease is increased in a marked manner by the addition of small amounts of alkali, the hydrolysis of part of the soap employed may be, therefore, considered to supply the alkali required to raise the emulsifying power above that which is inherent in the soap alone. If this were all that has to be considered, it might be expected that those soaps which are more readily hydrolysed than others would be the best detergents. This appears to be true in a general sense, so far as strictly comparable soaps are concerned—that is to say, alkaline salts of fatty acids of the same series (*e.g.*, lauric, myristic, palmitic, and stearic acids), provided equivalent quantities are taken, and the temperature of the water is warm enough to hold a reasonable amount of sparingly soluble soaps, like sodium palmitate and stearate in proper solution. But it would not necessarily be true to ascribe the rather greater detergent power of soaps derived from acids of relatively high molecular weight to their increased hydrolysis alone—*i.e.*, to the greater amount of alkali liberated by the action of water on them—for these soaps by themselves have emulsifying properties superior to the soaps of lower fatty acids, and also furnish a lather more readily if used under suitable conditions

Oleic acid, which belongs to another series of acids, furnishes soaps of considerable solubility in water, and potassium oleate is about two and a half times as soluble as sodium oleate. If equivalent quantities of these and of soaps from other common fatty acids are taken and a number of comparative experiments are carefully made, it will be found that the detergent properties of the oleates, both in cold and hot solutions, are sensibly the greater. This cannot be attributed to increased hydrolysis, which is about the same as that of some of the others in the cold, and becomes less as the temperature rises; moreover, the same superiority is found using equivalent amounts of the various soaps in solution in strong alcohol. The difference must, therefore, be due to the greater inherent emulsifying and perhaps lathering power of the oleates, and to other properties which will be dealt with presently. With regard to lathering, experience shows that a good washing soap should give a full lather, but this should probably be looked upon as a sign of other useful properties rather than as a necessity in itself.

So far, then, the behaviour of soap as a detergent has been ascribed to its own inherent power of emulsifying grease, aided by that of the alkali liberated by hydrolysis, the dirt being either carried away clinging to, or enclosed in, minute oily globules, or more frequently freed from a slight binding coating of grease, and removed separately in the soapy liquor.

of a so-called "basic soap." In experiments relative to this subject the author has found that solutions of free caustic alkali, as well as mixed solutions of caustic alkali and soap, do not cleanse wool as well as plain solutions of soap alone. It is the author's opinion that the cleansing action of soap solutions, or other solutions, is due almost entirely to the emulsifying quality of such solutions on the fats and greases which they remove.

Soap solutions have the peculiar property of closely amalgamating with greasy matters in such a manner as to cause the suspension of the grease in the form of finely-divided particles in the soapy liquors, and consequently facilitate the removal of such grease from the surfaces to which such solutions may be applied.

The cleansing action of solutions of alkaline carbonates and caustic alkalies, or of infusions of soap-bark and the like, is to be explained principally in the same manner. Where carbonated alkalies or caustic

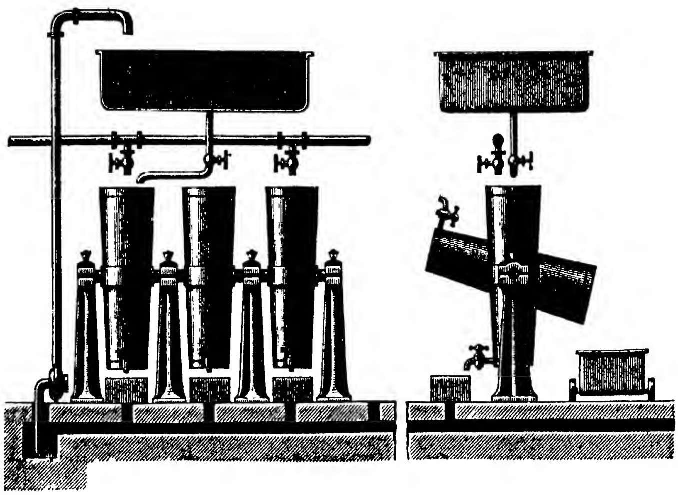

FIG. 7—Steeping Tank for Wool Washing.

alkalies are employed, there may be a small degree of saponification of the fatty matters, and consequently their cleansing action may to some extent be due to this formation of a soluble soap. If the cleansing action in such cases, however, was entirely due to this saponification, it would naturally follow that solutions of caustic alkalies would be better than soap solutions for the scouring of wool, apart from any action either may have on the fiber, and considered only with reference to their power of removing grease; but the author has shown by experimental data that this is not the case.[12] The cleansing action of such substances as fuller's earth mixed with water is also to be ex-

[12] See *Jour. Soc. Chem. Ind.*, 1905, p. 659.

plained by the emulsifying action such a mixture has upon the grease on the fiber. That is to say, the fuller's earth suspended in water in a finely-divided state mechanically decomposes the grease by friction into very small particles, and hence brings about the condition of an emulsion.

It has already been observed under the discussion of the chemical properties of wool-fat, that the greasy matters to be found on the fleece of the sheep are liable to contain a considerable proportion of free fatty acid. The neutralization of this fatty acid with the consequent formation of a soluble soap may in some degree aid in the after emulsification of the rest of the fat, but the cleansing action due to this cause must necessarily be but small.

The action of water on soap is as yet not thoroughly understood. There is, however, an increase in the alkalinity of a soap when dissolved in cold water, as may be shown by adding some water to an alcoholic solution of soap containing a few drops of phenolphthalein solution; as soon as the water is added the solution becomes red, showing the formation of free alkali. Wright and Thompson, in a series of experiments on the action of water on soap, give the following results of the amount of hydrolysis which occurs by using various quantities of water. The figures given are the quantities in percent of alkali in the soap. It is seen that tallow soap is less hydrolysed than palm oil soap, while cottonseed oil soap is more hydrolysed than any other.

HYDROLYSIS OF DIFFERENT SOAPS BY WATER.

		Mols. of Water.				
Soap from	Mol. Wt.	100	250	500	1000	2000
Pure stearic acid	284	0.7	1.0	1.7	2.6	3.55
Palmitic acid	256	1.45	1.9	2.6	3.15	3.75
Cocoanut oil	195	3.75	4.5	5.4	6.45	7.1
Pure oleic acid	282	1.85	2.6	3.8	5.2	6.65
Crude ricinoleic acid	294	1.55	2.2	3.0	3.8	4.3
Palm oil-tallow	271	1.1	1.55	2.6	4.1	5.3
Tallow and rosin	280	1.5	2.25	3.1	4.2	5.3
Cottonseed oil	250	2.23	3.0	5.0	7.5	9.5

According to the experiments of Krafft and Wiglow,[13] when hot one percent aqueous solutions of the following sodium soaps are allowed to cool, crystals begin to form at the temperatures given:

	° C.
Sodium stearate	60
Sodium palmitate	45
Sodium myristate	31.5
Sodium laurate	11
Sodium elaidate	35
Sodium oleate	0

All of these temperatures are considerably below the melting points of the corresponding fatty acids. The crystals appear to consist of a mixture of the normal and acid salts; when deposited from more

[13] *Berichte*, 1895, p. 2566.

dilute solutions, the crystals contain a smaller proportion of sodium, while from a 5 percent solution of sodium oleate, the neutral salt separates unchanged. If the hot, aqueous solutions are saturated with carbon dioxide and allowed to cool, the acid salts separate out, for example, sodium hydrogen palmitate, $C_{16}H_{31}O_2Na.C_{16}H_{31}O_2H$. The same chemists have made an examination of soaps with respect to the extent to which they raise the boiling-point of water. Sodium acetate and propionate (the lower acids corresponding in chemical constitution to the higher fatty acids contained in soaps) act as if each molecule were dissociated into two. Sodium palmitate, stearate, and oleate at first produce a rise in the boiling-point, but eventually, as the solutions become more concentrated, the thermometer falls to the boiling-point of the water, and the solutions solidify on cooling to gelatinous masses. Soaps under these conditions do not raise the boiling-point of the water in which they are dissolved, and thus exhibit the behavior of colloid substances like starch and gelatine.

It has often been stated that potash, and not soda soaps, should be used for the scouring of wool, and that the former yield better results in every way, the wool being left in its original soft and springy condition. This may very likely be the experience of many wool scourers, but it is doubtful whether the results, if superior, are to be considered as due to any special properties of potash soap as such. Careful comparative experiments with potassium, sodium, and ammonium oleates in a practically neutral condition do not show an appreciable difference in the behavior of the three soaps, so far as the final condition of the wool is concerned. It is possible that the advantage believed to be connected with the use of soft soap for wool may be due rather to the greater solubility of potash salts of mixed fatty acids, admitting of the use of more soap at a lower temperature, to the small amount of free alkali which used to be present as a rule in the older forms of soft soap, and to the fact that soft soaps were at one time made from oils which contained a high percentage of glycerin compounds of oleic and analogous acids. It is certainly very doubtful whether some of the soft soaps which contain much free alkali could, in any hands, yield such good results as a neutral oil or tallow soda soap of high quality. It has been suggested that the glycerin present in soft soaps has some good effect on wool, but it is difficult to see what beneficial action it can have during the washing process. It is sometimes the custom, however, to avoid rinsing out the soap completely from wool, and it is possible that the small amount of glycerin left in as well may tend to keep the fibers pliable, but the amount is very small, and just as good results can be obtained with copious rinsing, or with neutral soaps free from glycerin.

In most establishments, especially in America, a previous steeping of wool in hot water is not resorted to;[11] hence the soluble potash salts

[14] When the raw wool contains a high proportion of dirt and sand it is not advisable to enter it directly into the scouring machines as the soap liquors would rapidly become too dirty for economical use. With such wools as Silesian, Saxony, and Botany wools, of the Australian type, steeping is not essential, but the coarser and wilder breeds should always be given this preliminary cleaning.

naturally existing in the suint of the fleece are still present in the scouring operation, and pass into solution in the scouring liquors. It has been thought by some that the presence of these soluble potash salts aids considerably in the removal of the greasy matters, and consequently by omitting the previous steeping of the wool it will not be necessary to use so much soap and alkali in the scouring. It has already been pointed out,[15] however, that this idea is erroneous, for the potash salts as they occur naturally in the suint of the wool are not present as the alkali potassium carbonate, but as salts of potassium with various acids which have little or no alkaline action. The presence of these potash salts in the scouring liquors, instead of increasing the effectiveness of the latter, tend to diminish it by lessening its emulsifying qualities. In reality, their presence causes a more or less "hardening" of the water and a consequent neutralization of some of the scouring power of the soap.

5. The Emulsion Process: Scouring by Means of Soaps and Alkalies.

In this method, the raw wool is nearly always scoured in a liquor containing mixed solutions of soap and alkali; it is seldom, if ever, that a soap solution alone or an alkali solution alone is used. If the wool is of a very dirty character—that is, if it contains large quantities of sand, dust, etc.—it is best to first wash it in a bath of cold, or preferably, lukewarm water, so that the majority of the miscellaneous dirt may be removed; otherwise the scouring liquors will soon become so charged with earthy matters as to be unfit for further use. In a fair sample of wool about 25 percent in weight will be removed by this preliminary washing, and as the wash waters are of no especial value, they may be run to waste. Where the wools to be scoured are not particularly dirty, or have been already washed on the back of the sheep before shearing, the preliminary washing operation is omitted, and the wool is placed directly in the scouring bath.

6. Nature of Alkalies in Scouring.

The nature of the alkalies employed in the scouring bath for raw wool, together with the strength of the solution, will largely depend on the character of the stock to be scoured. The coarser and less lustrous the fiber, the more severe may be the scouring; while finer and more lustrous qualities of wool must be handled with greater precaution, in order to prevent the fibers from becoming matted and from losing their luster. The usual materials employed for scouring are soap and the two carbonated alkalies, soda and potash. As already mentioned, a mixture of soap and alkali is nearly always used, and the greater the amount of the alkali, the more severe will be the scouring; whereas soap has a milder action.

It is a mistake to conclude that the dirtier and greasier wools should be treated with the stronger scouring baths, for, as a rule, the finer grades of wool contain a larger amount of grease and dirt than

[15] See page 25.

the coarser varieties; so the strength and character of the scouring bath must be determined by reference to the quality of the wool, and not necessarily by the amount of grease and dirt on the fiber.

With respect to the alkali used, it is generally considered that potassium carbonate (pearl ash or potash) is more efficient than the corresponding sodium carbonate (soda ash), and that the former is also less harmful in its action on the wool fiber. This, however, is a matter open to much discussion. Expressed in terms of its "causticity" or intensity of action chemically, potash is stronger than soda, as potassium is a more basic element than sodium; therefore it is hard to explain why so many scourers consider the former compound a "milder" alkali than the latter. Expressed in terms of its neutralizing power (with respect to acids), potash is weaker, weight for weight, than soda ash, and this may have something to do with the supposed greater mildness of the former salt. In place of the true carbonates of the two alkali metals mentioned, their bicarbonates are also used at times in the scouring baths to replace the carbonates themselves, either partially or wholly. By some, the use of bicarbonates is considered as advantageous in that the alkaline action is milder and the scouring equivalent is greater, or at least equal to, that of the carbonates. Carbonate of soda is a salt of carbonic acid (H_2CO_3) in which both of the hydrogen atoms have been replaced by a like number of sodium atoms; in other words, the acid is completely neutralized by the base. Bicarbonate of sodium, on the other hand, is a salt of carbonic acid in which only one of the two hydrogen atoms of the acid are replaced by a sodium atom; that is to say, the acid is only half neutralized by the base, and therefore the alkalinity of the bicarbonate is only one-half that of the carbonate. That the former is a "milder" alkali there can be no question; but if we are to consider the scouring equivalent to be measured by its alkalinity, then the bicarbonate cannot be said to be more than one-half as efficient as the carbonate. As with soaps, however, the emulsifying equivalents of these salts has never been studied, and until some demonstration of this property of the two salts with respect to scouring has been made, it will always be an open question as to their relative merits, which can only be decided by the individual scourer from his own practical experience. Further consideration of this subject will be taken up under the study of the nature and properties of the different scouring agents.

Ammonium carbonate and ammonia are employed in some mills on very fine grades of stock; their price alone prevents their general application as scouring agents.

König [16] recommends the use of ammonia soap for wool washing, such soap being formed spontaneously in the fiber during the process, which is as follows: In the first vat the wool is washed with dilute ammonia, pressed through squeeze-rolls, then saturated with olein and scoured again with warm water (120° F.) and ammonia solution. In this manner it is claimed that an ammonia soap is formed very homogeneously throughout the fiber, and it becomes particularly effective in

[16] *Ger. Pat.* 146.052.

the emulsification and removal of grease. The material is passed through squeeze-rolls again and for a third time scoured with dilute ammonia water, and finally rinsed in plain water. While such a process might be useful for fine wools it would be far too costly for the ordinary grades of raw wool.

A novel method for the scouring of wool with soap liquors is the process of Schmid[17] in which the material, instead of being treated with a solution of soap directly, is subjected to the action of the foam or lather of the soap, this being produced by a vigorous boiling of the soap liquor. A suitable apparatus is employed so that the material is held in a receptacle above the surface of the soap solution so that it only comes in contact with the foam. It is claimed that this process requires less time and gives a very thorough cleaning with less felting of the fiber. The process is really an extension of the Schmid method for degumming silk, and though in the latter case it appears to have become somewhat of a commercial success, it does not seem to be of any great value for the scouring of wool.[18]

7. Nature of Soaps for Scouring.

The question as to the relative value of various soaps in scouring is a difficult one to decide with any degree of accuracy, and there is no scientific data on the subject which one may use for its proper elucidation. The scourer must base his ideas upon his own practical experience in the use of different kinds of soaps and a comparison of the results obtained. It appears to be generally admitted in practice that soft potash soaps are more efficient than hard soda soaps; probably this is due to the more thorough solubility of the soft soaps in water at the temperature at which the scouring is conducted; for, on the other hand, there is less actual soap, weight for weight, in soft soaps than in hard soaps. Until a proper expression, however, can be given to the emulsifying power of soap solutions, and an accurate method devised for the determination of the same, this question as to the relative value of soaps for scouring purposes will always be open to discussion.

8. Temperature in Wool Scouring.

Especial attention should be paid to the temperature of the scouring bath. This should not be allowed to rise above 140° F. under ordinary conditions, as alkaline solutions have an injurious action on the wool fiber at elevated temperatures, causing it to become considerably weakened both in tensile strength and elasticity, while at the same time the luster is greatly impaired, and the "feel" of the fiber becomes harsh and unpleasant. If the scouring solution contains too great a proportion of carbonated alkali, the wool is also liable to acquire a yellowish color which cannot afterwards be removed. Where the proportion of soap in the scouring bath is greater and a minimum amount of alkali is employed, a higher temperature may then be used than otherwise, but it will not usually be required to raise the temperature above

[17] *Fr. Pat.* 407,596.
[18] *OestErr. Woll. und Leinen Ind.*, 1910, p. 1143.

140° F. to thoroughly and efficiently cleanse the wool.[19] The object of using warm rather than cold baths in the first place is to soften the greasy matters on the fiber so that they may be the more readily removed; and secondly, on account of the more ready solubility and lower viscosity of soaps in hot water. The emulsifying power of soaps appears to be much greater in hot solutions than in cold.

Formerly it was common for the scourer to gauge the temperature of the liquor by his hand, and this practice has not even yet been completely abandoned. It is bad, since the temperature will feel to be quite different to two different persons, and to persons in different degrees of health. The thermometer should be the only means of gauging the temperature. For the ordinary run of Colonial wools temperatures of 120° F. in the first bowl, 115° F. in the second, 105° F. in the third, and 100° F. in the fourth bowl usually give very satisfactory results; while for very dirty, waxy wools, such as Buenos Ayres, a temperature as high as 135° F. is often required to start the grease. When washing the best English luster wools and mohair, the temperature should be as low as possible consistent with efficient scouring; temperatures ranging from 100° to 90° F. usually give good results. In all cases it is better practice to spend more time in scouring and keep the fiber sound than damage it by too hasty scouring and be compelled to spend more time in preparing, spinning, and felting; since, if scouring is done too quickly with too strong solutions and at too high a temperature, the serrations are damaged by being broken or "hacked," the luster is seriously impaired, and the fibers are rendered brittle and harsh in handle. The strength of the scouring liquor is quite as important as the temperature, and should in all cases be regulated in accordance with the fineness of the wool to be scoured, rather than by its condition with regard to the amount of dirt and yolk it carries. A coarse, strong wool will stand a greater heat and stronger scouring liquor than a fine and comparatively weak wool. In the first bowl, when washing very greasy cross-bred wools, it is usually necessary to use from 60 to 80 lb. of pearl ash, enough neutral potash soap being added to make the liquor feel sufficiently smooth and soft. For a fine wool rich in suint and yolk, and thus possessing a certain amount of cleansing agents, so strong a liquor is not necessary. Further, if the liquor were too strong, the handle and color as well as the spinning and felting properties would be seriously impaired.

[19] Turner (*Text. Mfr.*, 1921, p. 4) gives the following range of temperatures for scouring different grades of wool:

Class of Wool	Temperature Fahr.	Temperature Cent.
Red sandy wool	130°	54°
Ram's wool	130°	54°
Fine Colonial greasy merino	120° to 130°	49° to 54°
Slipe wool (lime pulled)	125°	51°
Skin wool (acid pulled)	120°	49°
Red lamb's wool	120°	49°
Medium cross-bred wool (Colonial)	115° to 120°	45° to 49°
Luster wools	100°	37.5°
Ordinary lamb's wool	90° to 100°	34° to 37.5°
Alpaca	80°	27°
Mohair	70°	22°

9. Strength of Scouring Baths.

As the strength of the scouring bath will depend on the quality of the wool to be scoured, no rigid and invariable formula can be given for the preparation of such liquors.[20] For ordinary grades of wool, it may be said in general that for every 100 gallons of water employed in the bath, from 2 to 10 pounds of soap and from 10 to 20 pounds of carbonated alkali are used for the scouring of raw wool. The quantity of soap to be used will also depend in some measure on the nature and quality of the soap employed.[21]

Scouring baths which have been in use for some time (provided they have been kept up to their proper strength by fresh additions of soap and alkali and have not become too highly charged with dirt) appear to be more efficient than those which have been freshly prepared. The reason for this is probably due to the fact that in the old baths the lime and magnesia compounds in the water have all been precipitated, and also that a certain degree of fermentation has arisen from the decomposition of the animal matter accumulating in the bath, which accelerates the removal of fatty matters from the fiber. Another reason may be that the presence of the wool-grease in the bath may aid somewhat in the emulsification of further quantities of grease from fresh lots of wool. Attention, however, must be called to the fact that in time the scouring baths will become foul by reason of the above-mentioned fermentation, and this will lead to the decomposition and destruction of the soap, which will weaken the bath for scouring purposes and also cause the wool to become foul in like manner. Therefore, when any evidence is shown of the bath becoming foul (which may easily be recognized by the disagreeable odor) it should be run off and replaced by a fresh bath.

Turner[22] gives the following interesting particulars concerning the practical scouring of wool. On a record kept of 14 lots of various grades of greasy wool, the following figures were obtained:

Total weight of greasy wool	11,000 lbs.
Total yield of clean wool	7,476 "
Average yield	67.9 percent
Maximum yield (pink blend)	84.0 "
Minimum yield (greasy gray brokes)	40.8 "

[20] For wools shrinking less than 50 percent the scouring bath should contain 3 to 5 lbs of soap per 100 gallons of water, together with 1½ lbs of soda ash for each 10 percent of shrinkage Coarse wools and those shrinking more than 50 percent may require a scouring liquor containing 5 to 10 lbs of soap per 100 gallons of water with a proportional increase in the amount of alkali.

[21] The amounts of soap and alkali used per day of ten hours in a set of scouring machines when washing an average greasy merino are: First bowl, 110 to 130 lbs. of a good potash soap and 20 to 30 lbs of pearl ash. Second bowl, 60 to 75 lbs. of potash soap and 3 to 6 lbs of pearl ash. (In some cases it should be noted that little or no alkali is used in this bowl.) Third bowl, 25 to 35 lbs. of potash soap Fourth bowl, 5 to 7 5 lbs. of soap or just sufficient to give the liquor a soft feel and neutralize and remove any traces of alkali which might still be carried by the wool from the previous bowls For washing very greasy cross-bred wools the amount of pearl ash used in the first bowl would be increased from 60 to 80 lbs, while the amount of potash soap used would be reduced to from 90 to 120 lbs In the second bowl 90 to 110 lbs. of potash soap and 10 to 20 lbs. of pearl ash would be used. In the third bowl only 30 to 45 lbs. of potash soap would be used; while in the last bowl 10 to 15 lbs. of soap would be used. The above particulars are for a set of machines of the same capacity as the set referred to in connection with the particulars given for washing merino wools. It should be noted that the particulars given can only be taken as a guide indicating quantities of detergents which may be used.

[22] *Text. Mfr.*, 1921, p. 43.

Actual consumption of soap....................................	128. lbs.
Actual consumption of soda ash................................	362. "
Time required for scouring...............................	13.23 hrs.
Soap used per pack (240 lbs.) greasy wool................	3.2 lbs.
Soda ash used per pack (240 lbs.) greasy wool..................	8.97 "
Time required per pack (240 lbs.)..............................	17.2 mins.

The scouring was done in a four-bowl machine, and the following particulars are given for the first lot:

WHITE HOG WOOL, 24'S COMBING QUALITY

	Start		Added	
Bowl	Soap buckets	Soda ash buckets	Soap buckets	Soda ash buckets
1	10	10	2	2
2	6	4	2	2
3	3	2	1	0
4	0	1	0	0

1 bucket of soap = 1.52 lbs.
1 bucket of soda ash = 2.88 lbs.
Time of feeding = 73 mins.
Greasy weight = 1000 lbs.
Clean weight = 802 lbs.

10. Effect of Scouring on Quality of Wool.

When scoured under the most favorable conditions by the soap and alkali method, the wool fiber will lose about twenty-five percent in tensile strength, and also somewhat is elasticity. The following figures are given as mean of a number of experimental determinations made by the author in this connection. The wool used was the kind known as "Territory ¾ blood."

	Tensile Strength	Elasticity
Wool in the grease..............	24.0 grams	28.0 percent
After washing in warm water............ ..	21.4 "	27.8 "
After scouring	18.6 "	26.2 "
Therefore:—		
Loss on washing........................... .	10.8 percent	0.8 "
Loss on scouring............................	11.7 "	5.6 "
Total loss	22.5 "	6.4 "

These tests were made on individual fibers, and a sufficient number of separate tests were taken to give a fairly accurate mean result; hence these figures represent the actual loss in tensile strength and elasticity of the fiber itself. Tests made with yarns (which will be given in a further section) would not truthfully represent this fact, as in the scouring operation, the individual fibers of the yarn become more or less felted together, and therefore, the strength of the yarn may become apparently increased instead of decreased by the scouring. The exact figures for the loss in tensile strength and elasticity will of course vary considerably with the nature of the fleece. The fine wools,

as a rule, lose more than the coarser ones, and there are other conditions of uncertain determination. The loss in strength is no doubt partially due to the fact that the layer of fatty matters and dried-up suint add somewhat to the solidity of the fiber, and help in some degree to cement the individual parts of the latter together.[23]

[23] Turner (*Text. Mfr.*, 1921, p. 4) gives the following practical general rules in wool scouring:

1. In wool scouring it should be the aim to produce well-scoured, bright, soft-handling, open-fibered wool in sufficient quantity to keep the carding engines and preparing boxes well supplied with wool, as "waiting" largely upsets the organization of even the most carefully thought-out plans of working.

2. Endeavor should be made to avoid matted, felted, stringy, and ropy wool, which is very difficult to operate in the after process, because it involves additional worry, expense, wear upon the machinery, and power in driving the machines. It also causes an extra amount of noil in the combing through excessive breakage of fiber, thus making the production of yarn a more costly process and sacrificing the quality.

3. Scouring should be done at the lowest temperature and speed consistent with good turn-oft, a lower temperature means softer wool, and low speed means less disturbance of the natural arrangement of the staple.

4. The brightness and color of scoured wool are two of its valuable properties, especially from the dyeing and selling point of view. They should be preserved as much as possible by refraining from the application of too high a temperature, too strong a scour, or too much alkali, in attempts to secure a large production from the machine.

5. It should always be remembered that if the wool is harsh or hard to handle, it entails the expense of adding olive oil and emulsions in order to soften the fiber to permit a good spin.

6. Proper care should be exercised in the economical use of water, soap, alkali, as the large quantities of these used entail heavy expense. Waste or carelessness of these essentials of the scouring process appreciably raises the cost of the resultant yarn.

7. It is desirable to have the machines adapted to suit the wool under treatment. They should be situated in a good light and be well supervised, kept clean, freely and regularly lubricated, and the parts properly adjusted and regulated. Steam and water joints should be tight and free from leakage. The machines should be mounted on good solid foundations. It is important to arrange that the wet wool from the scouring is rapidly passed to the drying machine, and is not left too long in the damp state. This causes the wool to become "stale" or "sad," and largely destroys its "spring" or elasticity.

Chapter IV.

Scouring of Wool (Cont'd).

1. Washing as a Process in Wool Scouring.

After the scouring operation has been completed, there is left in the fiber a large amount of soapy and alkaline liquor, together with the emulsified fatty matters and dirt which these absorbed liquors contain. It is very essential, therefore, that after scouring a thorough washing with warm water should follow for the purpose of removing these substances. Washing is an operation which should receive very careful attention, for if the fiber is not completely freed from all adhering soapy and fatty matters, bad results in the subsequent dyeing and finishing operations are almost sure to follow. Any soap which may become dried into the fiber is afterwards very difficult to remove, and may cause streaks and spots to appear, the true origin of which may frequently not be understood. Especially will this be the case if the wool is subsequently mordanted with metallic salts, as these form sticky insoluble metallic soaps which it is almost impossible to afterwards completely remove, whatever treatment may be adopted. Should soapy wool also be treated with acid solutions in dyeing or finishing, the soap will suffer decomposition with the formation of free fatty acid; and as the latter is insoluble and greasy in nature, its presence may lead to many bad results. Certain dyestuffs also form insoluble greasy precipitates with the fatty acids in the soap with the result that dark greasy spots will develop after dyeing.

Warm water is much to be preferred to cold in the washing of scoured wool, chiefly for the reason that if cold water is used some of the soap as well as the emulsified grease is liable to be precipitated from solution within the fiber, and greasy matters consequently be left in the wool; it is not necessary, however, that the temperature of the water should be over 120° to 140° F. Best results are probably obtained where the material passes from the main scouring bath into another weaker one, and then finally is washed with fresh water; this allows the concentrated soapy liquor to be removed in most part in the weak scouring solution, so that the subsequent washing is more certain and complete in its results.

2. Influence of Character of Water.

The character of the water employed in scouring and washing has a considerable influence on the good results of these operations. If the water is at all hard, the soap left in the goods from the scouring bath will be precipitated in the fiber and remain as an insoluble metallic

soap. The water employed in either scouring or washing should always be softened beforehand by the addition of the requisite amount of soda ash, or other alkali, after which it may be employed with impunity.

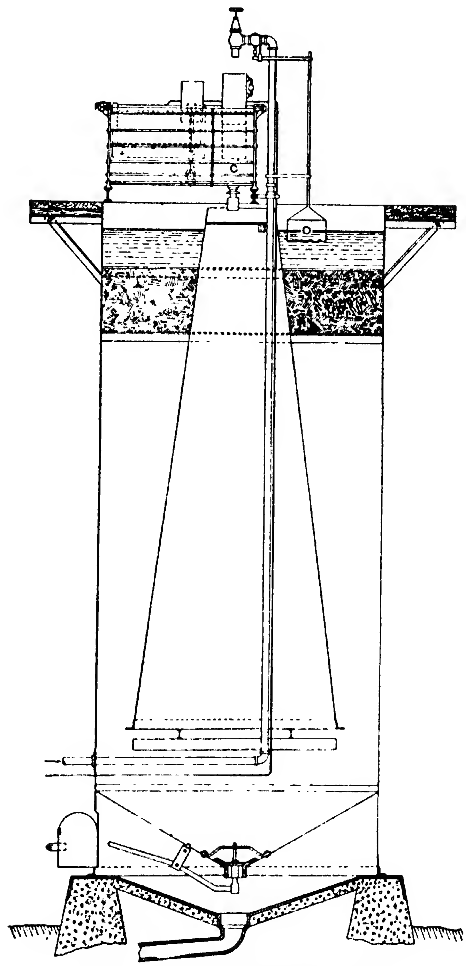

FIG. 8.—Kennicott Water Softener.

In scouring and washing, soft waters are always to be preferred and should be used wherever available; hard waters are frequently totally unfit for use; though in cases where no other kind of water is at hand, these may usually be softened in such manner as to be of use.

In the ordinary processes of scouring, bleaching and washing, the

use of water containing over 5 to 6 degrees of total hardness should be avoided, and water of greater hardness should be properly softened before use. For purposes of bleaching water should not contain a higher content of iron than 1 mgm. per liter (1 part per 1,000,000), as otherwise the tone of the bleached material is liable to be affected. The same is also true when water containing organic matter is used; this nearly always contains brown coloring matters that will be absorbed by the bleached fiber, resulting in a brownish or yellowish tint which is difficult to remove. Such organic matter, however, is usually rather easy to remove by the use of an alum coagulant and filtering; whereas the iron is sometimes more difficult to get rid of. Small amounts of potassium permanganate solution added to the water will also destroy the organic and coloring matters present.

To determine the availability of water for purposes of bleaching, place 250 c.c. of the filtered water in a porcelain dish and evaporate on a water-bath to 5 c.c. If the water left as a residue shows a yellowish or brownish color or sediment it may be considered as not sufficiently pure in quality for bleaching. The water sample after evaporation should also be tested for the presence of iron by adding a drop of nitric acid and a few drops of potassium ferrocyanide solution. The formation of a blue color will indicate the presence of iron.

The amount of water required in scouring and bleaching is very large in proportion to the weight of the goods being treated. For the scouring and bleaching of 100 lbs. of woolen goods, there will be required about 2000 gallons of water: 100 lbs. of cotton goods will require about 3000 to 4000 gallons of water, while 100 lbs. of linen will need about 10,000 gallons. These figures must be regarded as only average and approximate, as the quantity of water needed will vary considerably with the form in which the goods are bleached (loose stock, yarn, woven cloth, etc.), with the degree and nature of the bleaching operation, with the kind of machines employed and many other factors.

3. Hardness of Water.

The hardness of water is due to the metallic salts held in solution or suspension.[1] The salts of most common occurrence are the bicarbonates, sulfates, and chlorides of calcium and magnesium. These salts form insoluble sticky precipitates with soaps, and when adhering to the wool fiber are exceedingly difficult to remove. Besides this, their presence renders a considerable amount of soap worthless, as all of the metallic salts must first be precipitated before any of the soap becomes available for cleansing purposes. The hardness due to the presence of bicarbonates is said to be *temporary*, as it is removable by simply boiling the water. This is due to the fact that on heating bicarbonates are decomposed into free carbon dioxide gas and an insoluble carbonate;[2] the latter being precipitated in the form of a fine powder,

[1] Water containing less than 5 parts of mineral matters per 100,000 parts is considered as "soft" water. Each degree of "hardness" (in parts per 100,000) is calculated to destroy about 1 oz. of soap to every 35 gallons of water used.

[2] A. H. Allen (*Jour. Soc. Chem. Ind.*, 1888, p. 801) does not consider it necessary to assume the existence of calcium bicarbonate (which compound has never been isolated) in order to account for the solubility of calcium carbonate. He considers it probable that calcium carbonate is capable of existing in a soluble colloid condition.

and thus removed from action. This reaction may be represented by the following equation:

$$Ca(HCO_3)_2 + \text{heat} = CaCO_3 + CO_2 + H_2O.$$

The hardness due to dissolved sulfates and chlorides is said to be *permanent,* as it is not removed by simple boiling, consequently it is the more objectionable of the two. The amount of hardness may be estimated in a very practical manner by ascertaining how much of a standard soap solution must be added to a given quantity of the water in order to produce a permanent lather.

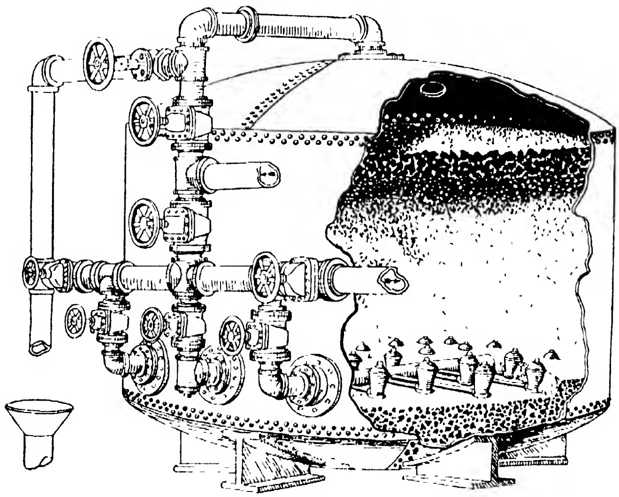

FIG. 9.—Showing Section of Sand Pressure Filter.

The quantity of calcium sulfate held dissolved in water is in general very much less than that of calcium carbonate, owing to the fact that carbonic acid has no effect on its solubility. Calcium sulfate is less soluble in hot water than it is in cold; Marignac found that 100,000 parts of water would dissolve the following amounts of calcium sulfate at the temperatures given:

32° F.	190 parts
104° F.	213 "
212° F.	173 "
284° F.	77 "
373° F.	18 "

It is very rarely that there will be found more than 10 grains of calcium sulfate per gallon in natural water; it is generally from 3 to 6 grains per gallon.

As a rule, the dissolved impurities in a water are of more importance than those which are merely mechanically suspended, as the latter

may be easily removed by either settling or filtering. Of course, if suspended matter is present in large amount, the water may be rendered unfit for use, especially if iron compounds are present. Water containing any considerable amount of iron salts in solution is called a *chalybeate* or *ferruginous* water, and is often highly prized for its therapeutic value. The iron is derived from beds of shale, and from coal and iron ore deposits with which the water may have come in contact. It is more apt to be found in spring water than in river water, as any salts of iron that may have come into the latter are soon changed to the insoluble oxide by the action of atmospheric oxidation. This oxide may often be observed settling out as a coating of iron-rust

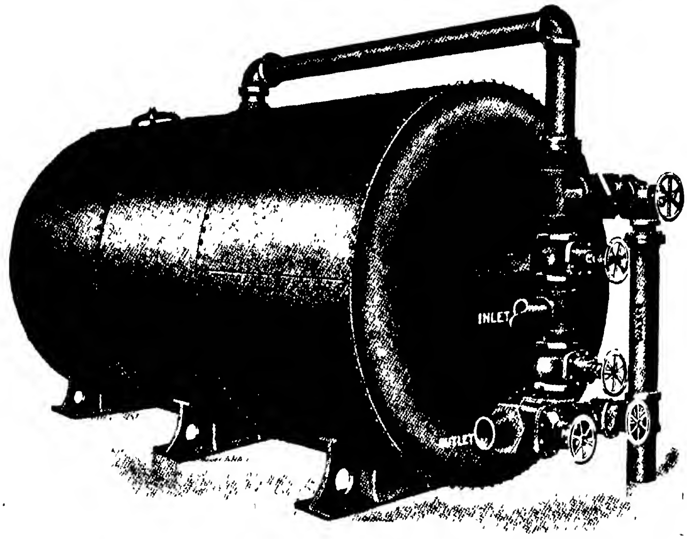

FIG. 10.—Horizontal Pressure Filter (Hungerford-Terry).

on exposed rocks in streams. River water containing much mud in suspension is generally liable to contamination with iron, and should not be used for either scouring or bleaching unless the mud is first settled out or filtered. River water is more apt to contain suspended matter than spring or well water; but, on the other hand, it generally contains less dissolved salts, since it is chiefly composed of surface water which has not percolated through the soil to any extent, and consequently has not had the opportunity of dissolving any appreciable amount of metallic salts. Rain water would be the best and purest form of water to use in scouring and bleaching; but, as a rule, its employment on a large scale is not practicable, owing to the limited and uncertain supply.

Water obtained from condensed steam which is sometimes employed for bleaching purposes is very soft and pure, being practically

distilled water. Unless proper precautions are taken, however, it is liable to contain oil which has been carried over with the steam. This is generally eliminated by passing the steam through proper oil separators. One serious defect of water obtained from condensed steam is the property it possesses of dissolving relatively large amounts of iron, so that if the condensation takes place in iron pipes and the water is stored in iron tanks, it will be badly contaminated with iron and hence be unfit for use in bleaching or scouring.

Besides the ordinary impurities mentioned in the foregoing paragraph, there is occasionally to be found either free acid or free alkali in water. Neither of these would have much influence on scouring operations, however, beyond the fact that any free acid would neutralize a corresponding amount of soap; whereas alkaline impurities would be beneficial instead of deleterious. Free acid in water may be either sulfuric acid or the so-called "peaty acids," which are organic. Sulfuric acid is formed in the decomposition of iron pyrites in contact with the water, and also by the oxidation of any dissolved ferrous sulfate, the iron oxide separating out and leaving free sulfuric acid in solution.[3] The organic acids are derived from the decomposition of vegetable matter, and are chiefly objectionable on account of their liability to hold iron in solution. The chief alkali to be found in water is sodium carbonate, and this is derived from the water percolating through certain coal measures. There are also certain districts in this country where considerable quantities of alkali are present in the soil, and water in these regions will, of course, be contaminated with this impurity. It may be easily corrected, if necessary, by the addition of the requisite amount of acid.

4. Faults in Scouring Due to Hard Water.

The frequent fault in dyeing known as dark and white *lists* is often due to the use of hard water for washing purposes. The goods after washing are rolled up and allowed to stand; the water at the edges evaporates, leaving any metallic salts in the fiber. The edges becoming dry draw out fresh quantities of water from the inner portions of the cloth by means of capillary attraction, and these fresh quantities of water in turn deposit their dissolved salts near the edges as exaporation continues. In this manner the selvedges become mordanted, as it were, while the inner portions of the cloth are comparatively free from deposited salts. When afterwards dyed such pieces will show light or dark streaks along the edges, depending on whether the metallic salts deposited there act as a resist or as a mordant towards the particular dyestuff employed. From the edge toward the middle of the goods there will be a shading, and if the piece has been standing on one end, there will be a heavier list at one edge, shading off gradually to the other.

If the goods are piled up in folds the edges of these folds will naturally be the portions which dry out the most readily, and this

[3] This acid will seldom be found in ordinary waters employed in mills.

condition will be liable to cause lists running directly across the cloth at more or less regular intervals.

In order to avoid the occurrence of these lists it is always best to cover the rolls or piles of cloth with a damp sheet whenever such cloth is required to stand for some time in the moist condition before it is dyed or finished.

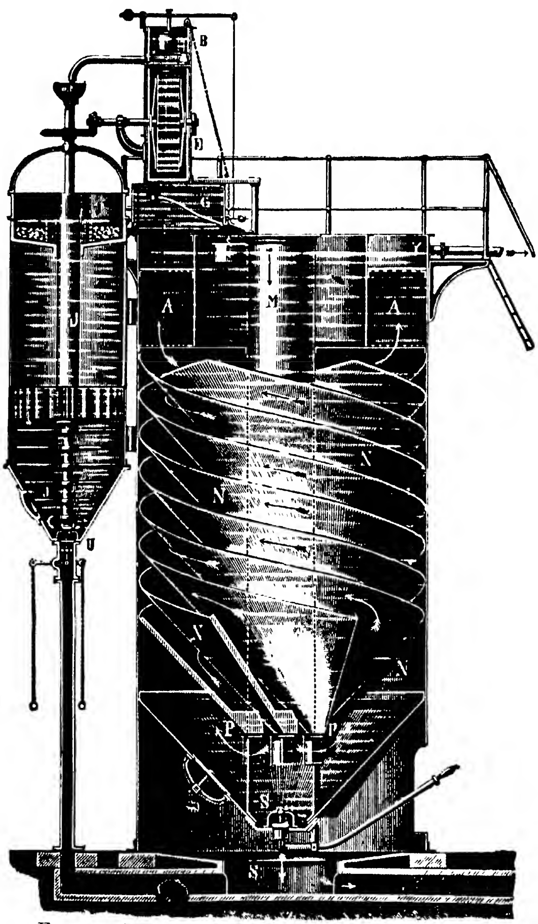

FIG. 11.—Eureka Water Softener (Dodge System).

5. Correction of Hard Water.

The correction of water for use in the textile industries is a question of considerable importance to the owner of a mill. As water is used so extensively and in such large amounts in scouring, washing, bleach-

ing and dyeing, it should always be one of the first objects of the manufacturer to locate his mill in a district where pure soft water is obtainable, if possible, thus doing away with the expense necessarily attached to the proper removal or neutralization of the impurities which may occur in hard water. The first order of impurities to be removed from water used for industrial purposes is that included under the general term of "suspended matter." As already mentioned, river

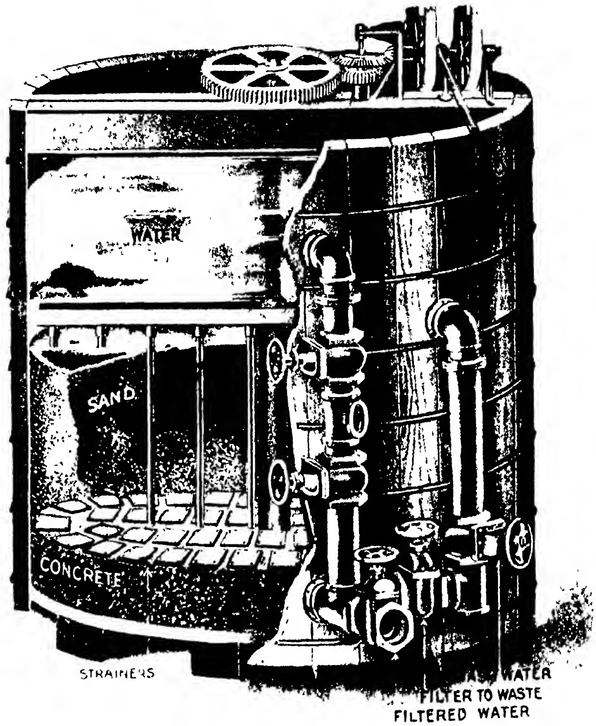

FIG. 12.—Section of Gravity Filter (Hungerford-Terry).

water is especially liable to this form of impurity; the amount, however, will vary within large limits depending on the nature of the land through which the stream is flowing, and also on the season of the year, heavy rainfalls, of course, largely increasing the contamination of the stream. Of all the impurities, however, to which water is subject, suspended matter is most easily and most economically removed. The best practice to employ is a satisfactory system of filtration, allowing the water to percolate through layers of gravel and sand. Sometimes, where such a system of filtration beds is not available, large settling

tanks are employed. The addition of a small amount of alum solution to the water greatly enhances the rapidity of its clearing, causing the suspended solids to separate out much more quickly. Such an addition, however, has the effect of introducing more or less of a soluble metallic salt (aluminum sulfate) into the water, and thus increasing its permanent hardness. Water to be used for scouring, washing, or bleaching, however, should be perfectly clear, even if it is necessary to use alum. The permanent hardness thus formed may be subsequently removed by use of a little soda ash. For use in scouring or washing water possessing any marked degree of permanent hardness may be best remedied by the addition of either caustic soda or soda ash in the proper amounts and boiling. In the scouring of wool, soda ash is a

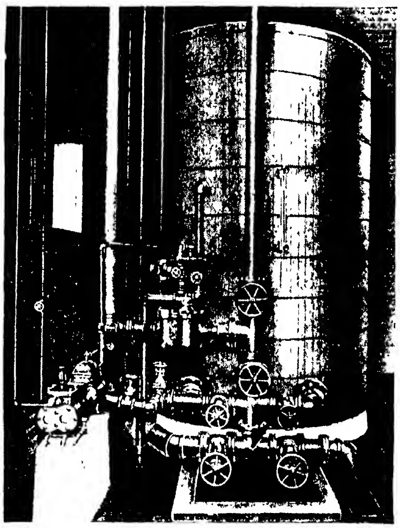

FIG. 13 Zeolite Gravity Softener (Permutit System).

safer remedy to apply than caustic soda, on account of the destructive action any excess of the latter would have on the fiber. In most cases it will hardly be necessary to filter or settle the water after adding the soda ash in order to remove the precipitated metallic carbonates; this is only required in practice where the water is exceedingly hard and the mass of the precipitate is considerable. Generally speaking, the precipitated carbonates are of a fine powdery nature, and form an inappreciable amount compared with the mass of the water treated, and have no effect on the soap solutions and do not present any difficulty in being washed out of the goods. Sometimes an insoluble scum will be formed on the surface of the liquid on boiling with soda ash; this should be removed by skimming. With water in which the hardness is principally due to calcium bicarbonate (temporary hardness), the most

economical method for correction is to add a small quantity of a saturated solution of lime, such a solution containing 1.3 grams of lime per liter. The softening in this case is brought about by the hydrate of lime combining with the bicarbonate present to form the neutral carbonate, which being insoluble is precipitated. To soften 845 U. S. gallons of water, about one ounce of quicklime will be required for each ten degrees of temporary hardness (parts per million). Excess of lime which may be inadvertently added may be precipitated by the addition of soda ash. The removal of calcium bicarbonate by such chemical means requires but little expense, as lime is quite cheap, and the amount required is very small. If calcium sulfate, however, is present (permanent hardness) then alkali must be employed, and this increases the cost of softening very materially. Water containing any marked amount of magnesium salts is also more costly to soften, as such water usually requires the addition of both lime and alkali. The

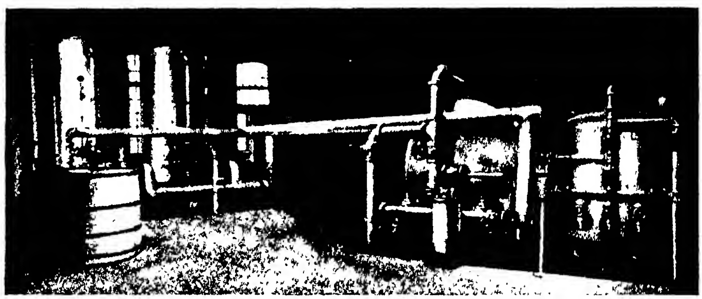

FIG. 14.—Zeolite Pressure Softener (Permutit System).

addition of oxalic acid to water to be used in the preparation of soap baths has been recommended as an excellent means of softening. In this case, the requisite amount of oxalic acid is added to the water together with the soda or potash, whereby an insoluble calcium oxalate is at once formed without the necessity of boiling. This is of a very fine powdery nature and presents no especial difficulty in being removed from the fiber by washing. After the oxalic acid has been added the soap solution is run in, and since all of the lime compounds have been precipitated, there will be no formation of insoluble lime soap. As the use of oxalic acid in this connection does away with the necessity of boiling and settling the water, it effects a considerable economy notwithstanding the higher price of the chemical employed.

Barium hydrate is another chemical employed for water softening, and although it is more costly than lime, it yields better results, as it removes the hardness without leaving any soluble salt in solution.

As far as the soap-destroying power of hard water is concerned, it may be stated that 1000 gallons of water will neutralize or precipi-

tate about 2.3 ounces of soap for each degree of hardness in parts per million.

Each grain of carbonate of lime per gallon of water causes an increased expenditure of about 2 ounces of soap per 100 gallons of water.[4]

When quicklime is added to water for the purpose of correcting hardness, it is essential that it be added in exactly the proper amount, for the addition of either a deficiency or an excess of lime may cause the water to become harder than it was originally. This is accounted

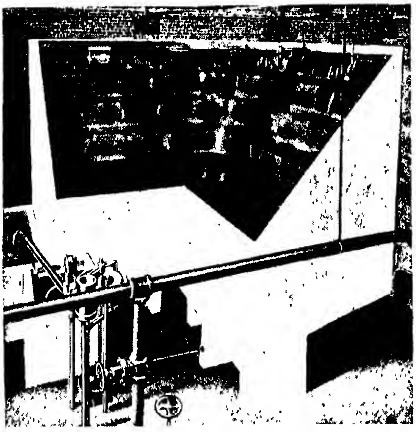

FIG. 15.—Aerator for Removing Iron (Permutit System).

for in the following manner: If the water under treatment contains any marked amount of dissolved carbonic acid gas, when too little lime is added it will be converted into the bicarbonate of lime, and consequently remain in solution and merely add to the hardness of the water. On the other hand, if the lime is added in too great a quantity, all of the carbonic acid is removed in the form of carbonate of lime and the excess of quicklime remains in solution, thus adding again to the hardness of the water. In order to know just what quantity of lime to add to any given kind of water, a chemical analysis should be made, and the proper amount carefully calculated.[5]

[4] *Eng. News*, April, 1892.

[5] In order to be able to calculate the quantity of reagent to be used for softening it is necessary to know the temporary and permanent hardness and the magnesia calculated into its equivalent of calcium carbonate. Pfeifer's formulæ may then be applied (Proctor, *Jour. Soc. Chem Ind.*, 1904, p. 11) as follows, the result being in pounds per 100,000 gallons. (Imp.) Let Ht = temporary hardness; Hp = permanent hardness; Hm = magnesia hardness; then

$$\text{Lime required} = 5.6\ (\text{Ht} + \text{Hm})$$
$$\text{Dry soda ash required} = 10.6\ \text{Hp}$$

For the removal of temporary hardness alone by means of lime, the quantity of lime required is 5.6 (Ht + Hm — Hp) when Hm is greater than Hp, or 5.6 (Ht + Hm) when Hp is greater than Hm In using caustic soda and soda ash the formulas are:

$$\text{Caustic soda required} = 8\ (\text{Ht} + \text{Hm})$$
$$\text{Soda ash required} = 10.6\ \text{Hp} - (\text{Ht} + \text{Hm})$$

When Ht + Hm is greater than Hp free sodium carbonate will be left in solution.

Iron and organic matter are also removed from water by the addition of either soda ash or lime, the iron being precipitated in the form of hydroxide, and carrying down with it most of the organic matter. When large amounts of organic matter are present it is advisable to add with the lime a solution of a salt of aluminum or iron, as the insoluble metallic hydrates which will thus be formed will also bring down the organic matter, and will also cause the carbonates of lime and magnesia to settle more rapidly.

When caustic soda is added to a hard water, it acts differently according to whether sulfate of lime (gypsum) or sulfate of magnesia

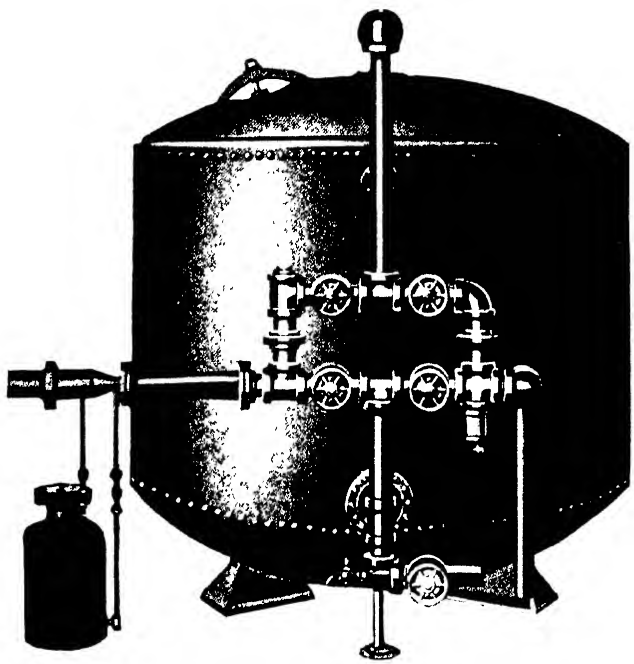

Fig. 16—Rapid Pressure Filter (Refinite System).

is present. If there is no dissolved carbonic acid in the water, the addition of caustic soda will not soften water containing sulfate of lime, as the only action taking place would be the formation of sodium sulfate and calcium hydrate, both of which remain in solution. Magnesium sulfate, however, will be precipitated as magnesium hydrate which is quite insoluble. If carbonic acid, however, is present in the water, either in the free state or as bicarbonate of lime, the addition of caustic soda will cause the precipitation of lime as calcium carbonate. If, however, carbonic acid is present in only small amount, or if the sulfate of lime is present in excess, soda ash must be added in connec-

tion with the caustic soda in order to precipitate all of the lime; this will also cause the precipitation of any magnesium salts. As the precipitates of lime and magnesium carbonates settle but slowly, numerous forms of apparatus have been devised for the purpose of increasing the rapidity of the settling. The principle in most of these is to give a large settling area for a small space, this being accomplished by a series of sloping shelves arranged within the apparatus, the water treated with the proper chemicals rising from the bottom of the tank and being drawn off from the top. The proper amount and exact nature of the chemicals to be employed can only be accurately determined after a chemical analysis of the water has been made.[6]

In the case of temporary hardness due to carbonates, 1000 gallons of water of 10° hardness (German scale) will require 15.6 ozs. (= 390 grams) of quicklime, or 22.3 ozs. (= 557 grams) of caustic soda for correction, in accordance with the following reactions:

$$Ca(HCO_3)_2 + 2\,NaOH = CaCO_3 + Na_2CO_3 + 2\,H_2O$$
$$Ca(HCO_3)_2 + CaO = 2\,CaCO_3 + H_2O$$

For permanent hardness due to sulfates, 1000 gallons of water of 10° hardness (German) will require 29.5 ozs. (= 737 grams) of soda ash for correction:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + NaSO_4$$

In case hardness of both kinds is present (as is most frequently the case) it must be borne in mind that if caustic soda is used to correct the carbonate hardness there will be some soda ash formed which will correct its proportion of sulfate hardness.

6. Softening with Zeolite.

Another method which is becoming rather extensively employed for the correction of hard water for textile and bleaching purposes is that using a mineral substance known as *zeolite*. This mineral occurs naturally and may also be made artificially. The latter product is known by the name of *Permutit*[7] and it is extensively used both in Europe and this country as a water softener. The zeolite is a mineral consisting of aluminum silicate combined with such other bases as sodium, potassium, calcium and magnesium.[8] The peculiarity of the zeolite is in the fact that if hard water (containing lime and magnesium salts) is filtered through a layer of the finely divided material

[6] The results obtained from soap tests are not as reliable as those from titration tests with acid, or better yet, a gravimetric analysis.

[7] The natural zeolite, obtained in certain parts of America, is also purified and used under the name of *Refinite*.

[8] The artificial zeolite or Permutit is made by fusing together feldspar, kaolin, clay and soda in definite proportions. The mass is then lixiviated with hot water for the purpose of hydration and for the removal of soluble silicates. The zeolite is left behind as a residue as a granular or flaky mass. It has a high porosity, and in the dry state will readily absorb as much as 50 percent of moisture. In the zeolite process for water softening a special installation containing apparatus for filtering, treating, and regenerating the zeolite is employed with proper means of regulating the treatment in accordance with the character and hardness of the water. The artificial zeolite, it is claimed, has the property of substituting one base for another to a much greater degree than the natural zeolites, exceeding by about 30 percent the capacity of Chabasite, which is the most active of the natural zeolites.

(usually in the form of small crystals) it exchanges its sodium and potassium radicles for the calcium and magnesium of the water, thus taking the latter compounds away from the water and replacing them with the alkalies. A further peculiarity, however, which allows of the practical use of the zeolite, is that after the zeolite has become saturated with lime and magnesia, by washing it in a solution of common salt, the lime and magnesia are removed and the sodium goes into their place in the zeolite; so by this means an easy method of regen-

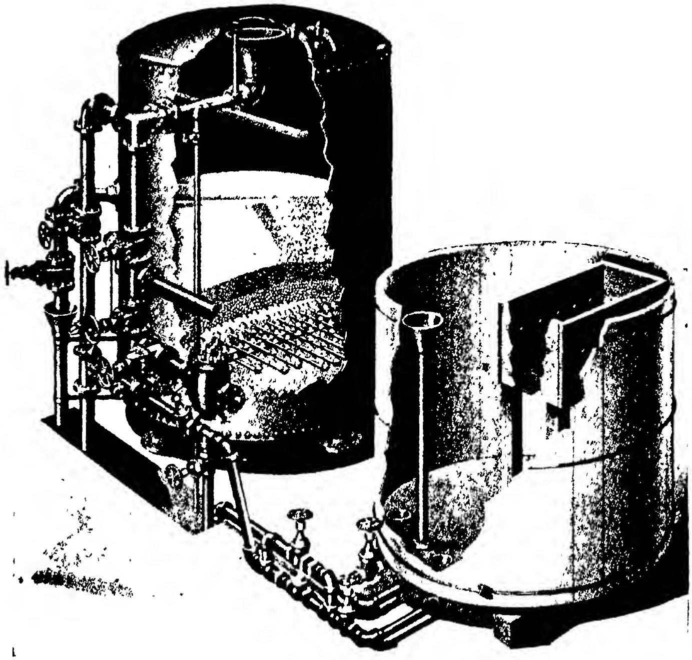

FIG. 17—Diagram of Zeolite Water Softener (Graver System).

erating the zeolite is available, and in consequence, it may be used continuously for softening an unlimited quantity of water, being successively regenerated by treatments with solutions of common salt. By this means of purification a water of zero degrees of hardness by the soap test may be obtained, which is scarcely possible by any other means. It must be borne in mind, however, that the water will contain sodium carbonate and sodium sulfate in an amount corresponding to the quantity of the carbonates and sulfates of lime and magnesia originally present in the water. As this process of water purification is simply one of softening by a chemical process, if necessary, the raw water should first be filtered before treatment with the zeolite in order

to remove sediment and insoluble impurities which would contaminate the softening medium.[9]

The zeolite process may also be used for the removal of iron from water in which case a manganese zeolite is used instead of the sodium compound. Water containing 1 part of iron per 100,000 when filtered through manganese zeolite gives a filtrate showing no trace of iron. The manganese compound is obtained by treating the sodium zeolite with a solution of manganous chloride.

In the zeolite installation for water softening the process provides for the filtration of the water through layers of the zeolite, the direction of flow being from the top to bottom, as this proves to be more effective. As the material tends to cake together somewhat in use, the mass is loosened up in the cleansing operation before each regeneration.

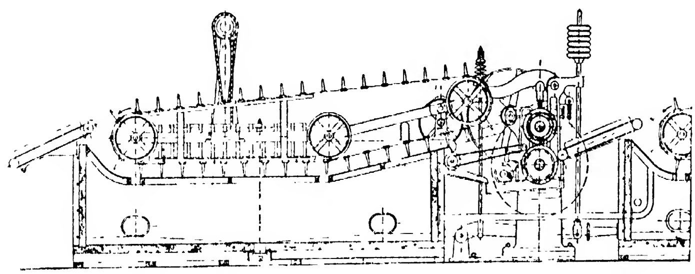

FIG. 18.—Electrolytic Scouring Apparatus for Raw Wool (Baudet System).

For this purpose soft water is used and the cleansing takes place from bottom to top, there being a good flushing and whirling motion of the water. The solution employed for regeneration consists of a 10 percent solution of common salt and is preferably used at a temperature of 100° to 120° F. This solution is allowed to flow slowly through the filter for from 4 to 5 hours. Mechanically impure water (containing suspended matter) must be previously filtered before being treated by the zeolite process. The water should also be neutral, that is to say, should not show an acid reaction with Pettenkofer's solution of rosolic acid. If this is not the case, the water must first be passed through a layer of broken marble in the filter.

7. Solvent Methods of Scouring Wool.

Although the method of treating wool with alkaline detergents for the purpose of scouring has been employed from time immemorial and is still the principal method in use, there is another process for

[9] Water softened by the lime-soda method (which has been the usual form of treatment) will seldom give a water of less than 3° of hardness; whereas the zeolite process will readily deliver water of zero hardness, and in some cases of scouring and bleaching this is of especial advantage. Unless a water of less than 3° hardness is desired, the lime-soda process is perhaps cheaper than the zeolite process. The exchange power of zeolite is about 1 percent, which means that 1 ton of zeolite is able to remove 20 lbs. of calcium oxide from the water.

wool scouring, radically different in principle but very effective, which is also being practiced to a considerable extent at the present time. It is a well-known fact that fats and greases, though insoluble in water, are readily and completely dissolved by such liquids as ether, chloroform, benzene, petroleum naphtha, carbon disulfide, carbon tetrachloride, etc. As these solvents are easily evaporated at comparatively low temperatures, they have received the general name of volatile solvents. Though long employed in the laboratory for the extraction of fatty matters, oils, etc., from a variety of substances for experimental or analytical purposes, their use in this respect for purposes of scouring wool on a commercial scale has only been taken up during rather recent years. As all of these solvents are of high price compared with soap solutions, their cost alone is prohibitory unless the solvent may be recovered without any considerable loss, and thus be

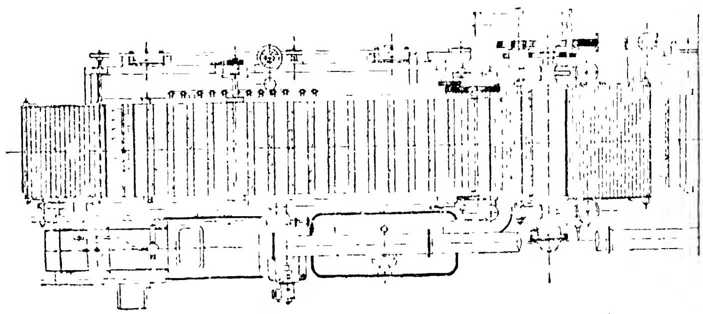

FIG. 19.—Top View of Apparatus (Baudet System).

used continually to extract the fat from fresh quantities of wool. Again, most of these solvents are exceedingly inflammable, and their vapors when mixed with air are highly explosive; consequently, there is considerable danger attending their use on a large scale, and the greatest care must be exercised in handling them. Moreover, the vapors from many of these solvents have an anæsthetic or a poisonous action on the human system, and on this account, beyond their liability to explosion, they endanger the lives of the workmen who have to carry out the operations involving their use, unless rigid precautions are taken to avoid inhalation of the fumes.

In recent years, however, the construction of suitable apparatus for the handling and recovery of these volatile solvents has been brought to such a high degree of perfection that the scouring of wool by means of volatile solvents is now carried out on a commercial scale with a minimum loss of solvent and with but little danger where the process is intelligently conducted.[10]

[10] The idea of degreasing wool by means of volatile solvents is by no means a new one. Attempts had long been made in this direction, but were usually unsuccessful owing to the extreme inflammability and explosive character of the solvents available (benzine, ether, naphtha, etc.) and the lack of proper control in the handling of these materials. On this account carbon tetrachloride was tried (the Peltzer patents) but proved to be too expensive

In principle, this method differs from the older process in that it removes the fatty matters from the wool in the form of a solution; hence it may be called a solution or solvent process in contradistinction to the emulsion process. Another essential difference in the two methods lies in the steeping operation; in the one, the steeping in hot water to remove the soluble compounds, if practiced at all, precedes the actual

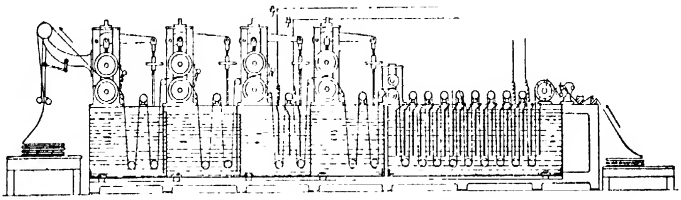

Fig. 20.—Electrolytic Apparatus for Scouring Woolen Cloth (Baudet System).

operation of scouring with soap liquors; whereas, in the second method, the steeping must follow the treatment with the volatile solvent, since the latter is not miscible with water, and therefore the action of the solvent would be ineffectual unless the wool were first dried after steeping, which would entail needless increase in time and expense.

The principal operation in the solvent process for the scouring of raw wool is first to remove the fatty or greasy matters by means of

for commercial use. Apparatus was devised to control the vapors of naphtha and benzine and the wool saturated with these solvents; but explosions often occurred due to the materials becoming electrically charged and producing a spark when near metal so that spontaneous explosion was developed. This led to methods for conducting the operations with total elimination of air by the introduction of an atmosphere of carbon dioxide gas. The present processes which have been so successfully operated in America have been made commercially possible by a highly refined engineering technique in the construction of suitable apparatus to handle the wool and the volatile solvent in an efficient and harmless manner, so that there is practically no danger of explosion and the loss in the solvent is very small. These factors have made it possible to scour wool with naphtha in a most effective manner and at a very low cost, while furnishing a valuable by-product in the form of wool-fat.

The early attempts at scouring wool with naphtha were not very promising, as the wool so obtained was harsher and more brittle than that scoured by the customary soap process in the Leviathan, and there was consequently a higher percentage of waste in carding and spinning. This was due to the fact that too much of the grease was removed from the fiber, and it was found necessary to so regulate the process that a small amount of grease or oil was left in the wool (see Kapff, *Farb. Zeit.*, 1902, p. 330).

In America the greater part of the wool scoured (at least for the manufacture of worsted tops) is probably done by the solvent process which is carried out at the extensive plants of the Arlington Mills at Lawrence, Mass., and Erben and Harding at Philadelphia. In Europe the process is carried out at Verviers, Belgium, also on a very extensive scale.

In addition to its use for the scouring of raw wool, the volatile solvent, or naphtha process is very extensively used both in America and Europe for the scouring of garments in the so-called "dry cleaning" method. For this purpose special installations of apparatus are available for use on a comparatively small scale. This method is practiced chiefly for the purpose of avoiding the shrinkage in garments and the bleeding of colors which nearly always occur when woolen materials are scoured by the soap and alkali method.

Associated with the volatile solvent process are also certain forms of soap containing naphtha or carbon tetrachloride or other similar solvents. Such products are Benzine Soap (made by emulsifying benzine or benzene (or benzol) with an alcoholic solution of soap), Benzoform and Tetrapol (soap compounds emulsified with carbon tetrachloride).

In order to prevent the formation of sparks due to electric discharges, and the consequent risk of explosions in dry cleaning with the use of naphtha or benzene it is customary to add to the solvent a small amount of magnesia soap (known as "Richterol" and also as "Antibenzenepyrin").

The following are some of the principal European patents relating to the scouring of wool with volatile solvents: M. Jacques & Co., *Ger. Pat.* 119,718; Peltzer & Co., *Ger. Pats.* 122,800 and 122,801; N. Rouselle, *Ger. Pat.* 117,727 (see also *Färb. Zeit.* 1901, p. 267); and Peltzer & Co., *Ger. Pat.* 160,375 (see also *Jahres Bericht*, 1905, p. 373).

certain suitable solvents, and after distilling off the excess of solvent, to remove the remaining impurities by treatment with water and soap. The success of the process largely depends on the mechanical contrivances necessary to carry it out, but the difficulties attending the perfection of these once surmounted, this method of scouring would appear at once the most logical in theory and the most economical in practice. For not only is the scouring agent employed in the process used over and over again with but little loss, but the products obtained in the scouring are also recovered in their entirety, and may be utilized for the preparation of many articles of commercial value.

The general procedure of scouring wool (the process is limited almost entirely to the scouring of raw wool) by the use of volatile solvents, is to place the wool in a suitable closed apparatus in which it may be steeped in petroleum naphtha (the most used solvent, on account of its comparatively low cost); all air being previously removed by use of vacuum. After the fatty matters on the fiber are dissolved by the warm naphtha, the wool is squeezed (while still in the closed apparatus) free from the solvent, rinsed with a fresh quantity of the naphtha to remove the last traces of the fats, and squeezed again. The residue of naphtha still in the wool is then removed by volatilization by careful heating, and the wool, completely freed from the solvent, is taken out and washed in warm water containing a small amount of soap in order to remove the soluble potash compounds together with the dirt. The naphtha, containing the wool-grease in solution, is run into a suitable still from which the solvent is distilled off and collected in cooled condensers, when it is again ready for use. That portion of the naphtha used for rinsing the wool after extraction is mixed with the fresh naphtha for use on further quantities of wool. The naphtha residues volatilized from the wool by heating are also condensed and run into the naphtha reservoir. In all these operations care must be taken to exclude air as far as possible, and also to guard against the ignition of the naphtha vapors by an electric spark or other source of flame. The wool-fat left in the stills is collected and sold; so it may be observed that in the solvent process of wool scouring the recovery of the wool-fat as a by-product is compulsory, and, in fact, pays the cost of scouring.

Benzine, or petroleum naphtha, has been the principal solvent employed, on account of its cheapness and general efficiency. Carbon tetrachloride would be an excellent solvent to use for this purpose, but its high cost at the present time is prohibitory; though this solvent is neither inflammable nor explosive, nor has it as pronounced anæsthetic properties as chloroform and other volatile solvents. It is to be hoped that processes for the manufacture of this substance may be discovered that will enable it to be made at a cost which will render it available commercially as a wool degreaser.

The solvent process for wool-scouring was long attempted in England, but for a long time without success; also on the continent of Europe there have been experiments leading to its use, but they seem to have been mostly abandoned without practical results. In the

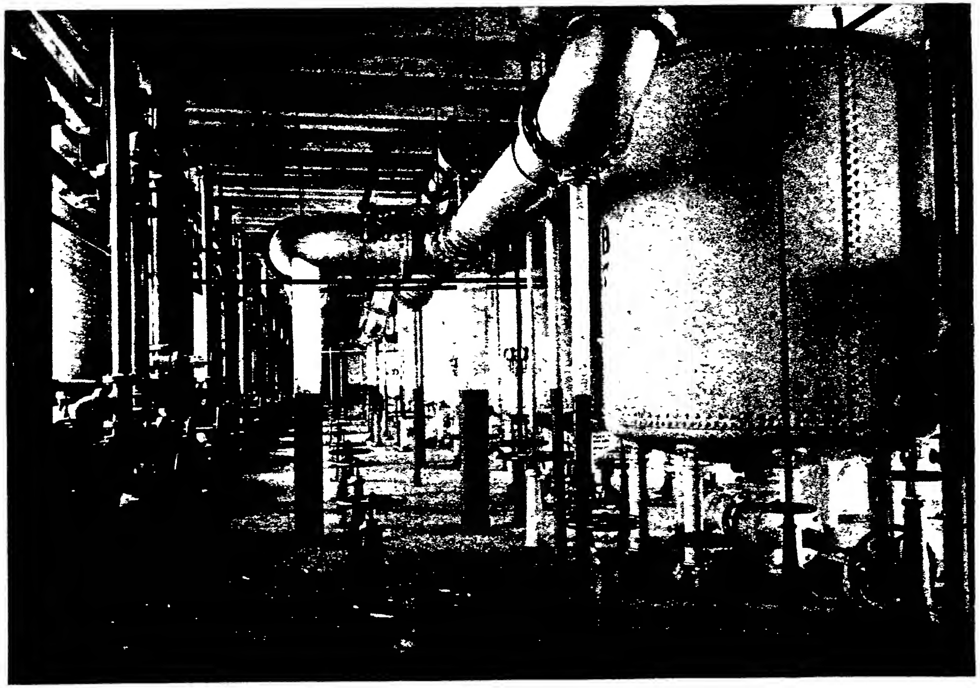

Fig. 21.—Showing Installation of Solvent Process for Wool Scouring (Arlington Mills).

United States, however, two of the largest wool-scouring firms of the country have been using this method for a number of years, and have successfully overcome all of the numerous practical difficulties of the problem, so that their wool is now scoured at a low cost and very efficiently.[11] The raw wool is placed in a kier, the top of which, on the inside, is provided with a heavy perforated cover; this is clamped securely, and then the top of the kier is screwed down. Suction is then placed on the kier, and the air is drawn out to a few millimeters vacuum; after this, the naphtha is admitted to the kier from the bottom at a temperature of about 100° F.; this is allowed to circulate through the wool for about half an hour, then a perforated plunger at the bottom of the kier is forced up at great pressure, whereby the naphtha containing the grease in solution is squeezed out of the wool, passing through both the perforated plunger and the perforated cover over the wool. This solution is pumped over to suitable stills, from which the pure naphtha is distilled off, leaving the wool-grease as a residue to be removed from the bottom of the stills. Clean naphtha is now admitted to the wool from the top of the kier, and the plunger is allowed to go down; this has the effect of drawing the clean solvent very completely through the wool. This naphtha is removed in the same manner as the first charge, and is pumped over to a reservoir to be used again on a fresh lot of greasy wool. The purpose of the second charge of solvent is to remove the last portions of adhering grease and greasy naphtha. Warm air is now forced through the wool and the plunger again allowed to fall; this serves to remove from the wool all the naphtha vapors. This air, rather heavily charged with naphtha, is passed through a catch-all in which most of the cooled vapors condense and are recovered; the current of air is then passed out to the atmosphere through a water-trap, which prevents any liability to fire or explosion. After all of the naphtha has been removed from the wool, warm water is admitted to the kier, and the wool is washed in order to remove the soluble salts. The water is squeezed out by means of the plunger, and then the wool is removed from the kier, and given a slight scouring in a weak soap bath for the purpose of removing the extraneous dirt. In this method of scouring the wool is left in an excellent physical condition, the fibers being free and open, and the luster unimpaired, and there is no felting and no breaking of the fiber by mechanical action. The naphtha is recovered very completely, the only small loss being some which remains in the wool-fat after distillation and that which is carried away in the form of vapor by the current of air which is passed through the kier. The time for scouring a 1,000-pound lot of wool in this manner is only from one and one-half to two hours, and the entire process is mostly automatic. All of the wool-fat is recovered, and has a ready sale in the market even in the crude condition; the wash waters are not worked up for the recovery of the potash salts. From the sale of the by-products, the cost of the scouring is entirely paid for, including the cost of the naphtha, labor, power, and interest on invested

[11] Reference is here made to the Arlington Mills, of Lawrence, Mass., and to Erben and Harding of Philadelphia. In the latter plant large iron kiers are employed, capable of holding 1,000 pounds of wool at a charge.

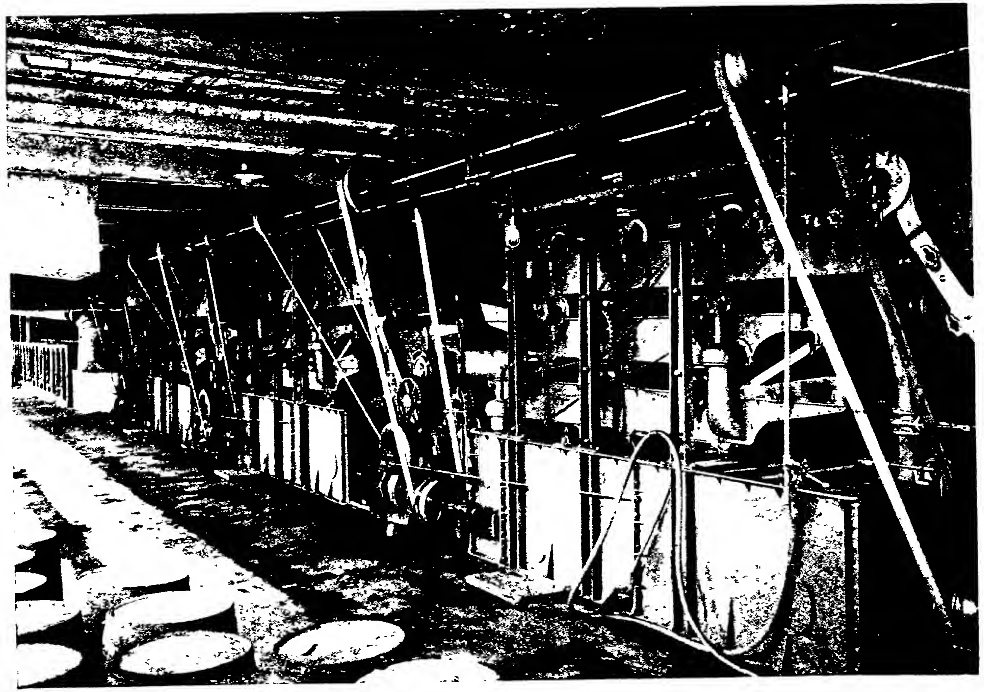

Fig. 22.—Showing Installation for Washing Wool after Solvent Extraction (Arlington Mills).

capital. From an experiment made on two lots of 25,000 pounds each, the one scoured by the usual soap process and the other scoured by the solvent method, and afterwards worked up through all the proc-

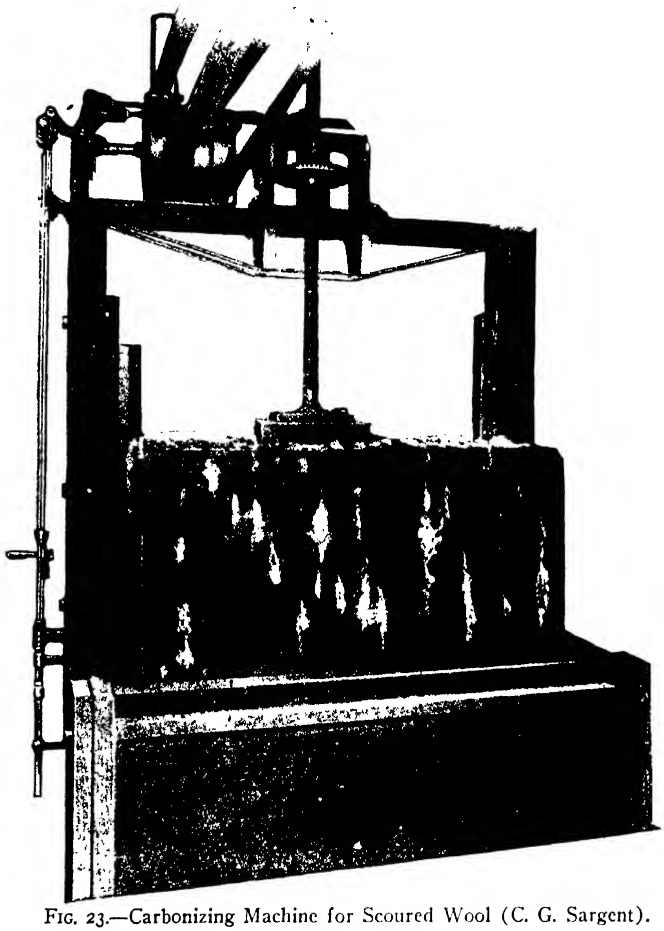

FIG. 23.—Carbonizing Machine for Scoured Wool (C. G. Sargent).

esses of carding, combing, spinning, weaving, etc., into the same class of fabrics, it was found that the wool scoured by the solvent process yielded about 10 percent more cloth in the end than the lot of wool scoured with soap.[12]

[12] In the Arlington Mills, instead of using a current of warm air for removing the last amount of naphtha from the wool, a current of warm carbon dioxide gas is used; this requires the additional cost of manufacturing and storing large amounts of this gas; but it is supposed that the use of such a non-combustible gas very considerably lowers the risk of explosion.

One of the dangers to which the solvent method of scouring is open, and in fact one to which any operation involving the use of benzine or other highly inflammable substance is subject to, is that of the benzine vapors being exploded by means of electrical discharges. This has been the cause of many fires and explosions in dry-cleaning establishments where benzine is employed for the cleansing of fabrics. An electric discharge or spark may be caused by the friction of the fibers or materials against each other or against the sides of the apparatus, and may take place when least expected. It has been found that by mixing a small quantity of soap with the benzine the electrical action is greatly reduced.[13]

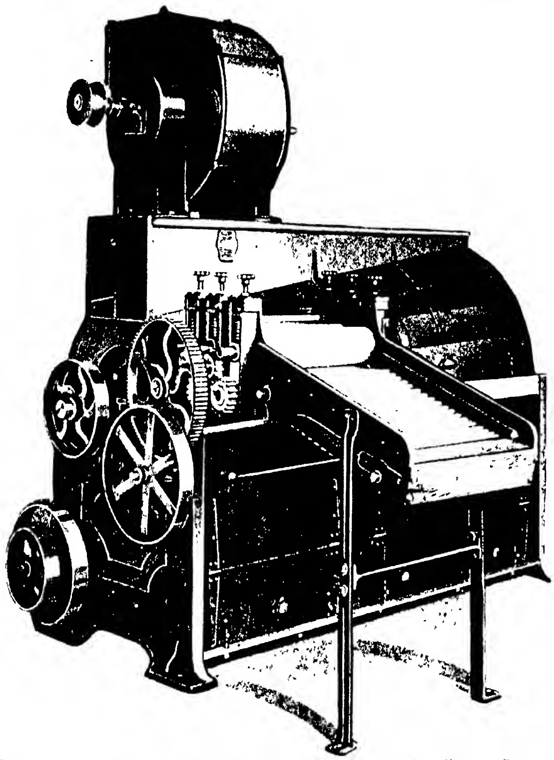

FIG. 24—Carbonizing Duster for Loose Wool (C. G. Sargent).

In the proper working of the solvent process, care must be had not

[13] A preparation for this purpose known as "Antibenzinpyrin" is extensively used, and has proved to be very efficient; it consists of 10 parts of magnesia soap (from rape-seed oil), 60 parts benzine, and 20 parts colza oil. (M. Richter, *Ger. Pat.* 83,048 of 1893). Another product of similar nature is known as "Saponolein," which consists simply of a solution of ordinary soap in benzine or other suitable solvent. (R. Gartenmeister, *Ger. Pat.* 87,274 of 1894.)

to remove absolutely all of the greasy matter from the wool. As already mentioned, the grease contained in the wool is supposed to be of two forms, that which acts as a protective coating on the fiber, and which forms the great bulk of the grease, and that which acts as a lubricant within the fiber, and which is only present in small amount. If the latter is removed as well as the former, the wool will become harsh and brittle and without life or elasticity. In order to preserve the good qualities of the wool, it is necessary that this small amount of lubricating oil be left in the fiber; this amounts to from one to two percent. In the ordinary soap-scouring method it is not often that there is danger of removing this lubricating oil, but in the solvent method it is very easily extracted unless the proper conditions be maintained.

The plant of Maertens' degreasing system [14] consists principally of underground reservoirs containing the naphtha; digesters, coupled together, which are also sunk into the ground, each of which is capable of holding about 3000 lbs. of wool; a gas-holder containing non-inflammable gas, and a compressor capable of driving the gas through the naphtha reservoirs and digesters; oil condensers which are placed above the digesters, and through which the gas passes on its way back to the holder. These extract and collect from the gas the naphtha vapor. An air blower, heater, and humidifier are also provided, by means of which a current of warm moist air can be circulated through the digesters and forward through a condenser back to the blower. The air is circulated through the digesters to extract the solvent naphtha. The action is briefly as follows: Compressed gas is turned into one of the reservoirs containing naphtha which has been used twice before, thus flushing dirty naphtha through the first digester. The naphtha is then carried away from the digester through a pipe connection to the distillery, where the naphtha and grease extracted are separated. Gas is next turned through the second reservoir, and naphtha which has been used once before is forced through the second digester and then through the first, from which it passes to the distillery. Clean naphtha is next flushed through the first digester from a clean naphtha tank, or reclaimed naphtha is used from the distillery. After leaving this digester it is flushed through the second, from which it is passed to one of the reservoirs. The second digester is now flushed with clean naphtha, from which it is passed to the other digester. The propelling or compressed gas is allowed to go back to the gasholder over the oil condensers, which collect the naphtha vapor and send it back at intervals to the distillery, where the naphtha is reclaimed. Finally, moist warm air is circulated through the digesters to extract all the naphtha vapor, but leaves the wool in normal condition as regards the amount of moisture it contains. A condenser is placed between the blower and humidifier for the purpose of extracting and collecting the naphtha vapor. By this means all the naphtha is reclaimed, and can thus be used repeatedly with very little loss. The flushings follow each other

[14] In use in Belgium.

in quick succession—almost as fast as the valves can be turned. The wool when taken out is simply rinsed, no real washing being necessary. This operation dissolves all the potash, and the wool is delivered from the operation of rinsing in an open, free, and clean condition, and retaining all its natural characteristics. The principal advantages of the system of scouring by means of volatile solvents are that it is a quick and very cheap method; a good income is derived from recovered potash and grease, the latter being purified according to requirements; the reagents are used repeatedly, and the valuable by-products are easily obtained. The agents used have no deleterious effect on the wool, and the wool is not submitted to the harmful effect of high tem-

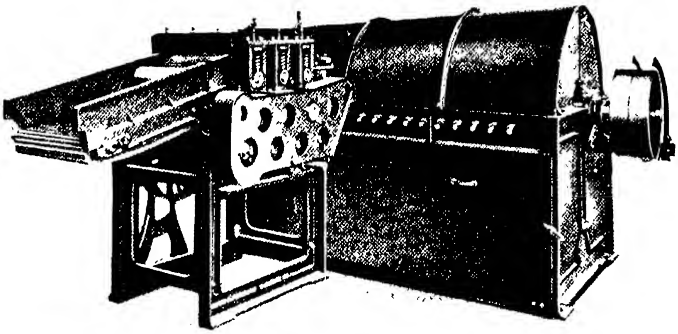

FIG. 25.—Carbonizing Duster with Crush Rolls (Smith & Furbush).

perature. The principal disadvantages are: The difficulty of dealing successfully with large quantities of highly inflammable and explosive liquid; large insurance premiums must be paid; and the initial cost of the plant is considerable. There is also a certain loss of the agent used, due to frequent distillation; this, however, is a minor detail.

8. Electrolytic Method of Wool Scouring.

During the past few years a new method of scouring raw wool and woolen cloth has been introduced depending on the treatment of the material with an electrolyzed solution of sodium carbonate. A special apparatus is employed so that an electric current is passed through the material while it is immersed in the alkaline solution, and it is claimed that in this way the fiber is subjected to the very intimate action of the electrolyzed alkaline liquor so that a highly efficient cleansing action is obtained. The following is a description of the Baudot process and apparatus: For the scouring of cloth the machine shown in Figure 20 is employed. The electrolytic vat is first charged with a solution of sodium carbonate of 3 to 4° Bé. at a temperature of 95°F., and then the electrodes are connected with a dynamo furnishing a current of 400 amperes and 4 to 5 volts. The fabric to be treated is entered into the electrolytic bath after passing over the stretcher and the feed

roller and then passes between each series of positive and negative electrodes. The current thus traverses the fabrics and sets up an electrochemical action within the fiber. After passing through the electrolytic bath the cloth is passed between the squeeze rolls and then into the bath which contains the soapy compounds resulting from the previous operations. The cloth then passes through a series of washing tanks and

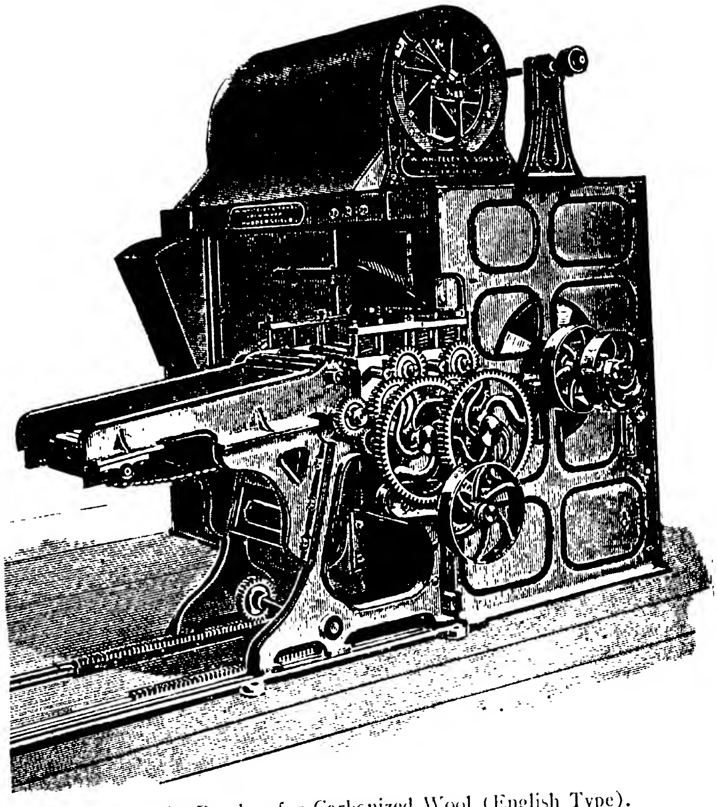

FIG. 26.—Breaker for Carbonized Wool (English Type).

squeeze rolls. The machine is run at a speed to deliver about 10 yards of cloth per minute.

In the treatment of raw wool by the Baudet process the apparatus shown in Figure 18 is employed. The wool is introduced by a feed table and by the endless traveling rake is carried over the perforated false bottom of the scouring bath; the middle portion serves as a negative electrode while the moving parts form the positive electrode; wooden insulators are used at suitable positions. After passing through the bath the wool is squeezed by rollers, the greasy liquors collecting in

the vat shown in Figure 19. The wool passes on to a second similar machine and then through two washing vats containing soap liquors which completes the scouring operations.

Very interesting results are claimed by this method of treatment, a superior quality of fiber is said to be obtained and a saving of 60 percent in the consumption of soap. In the electrolytic vats the scouring is accomplished solely by means of the electrolysis of the salts contained in the suint of the wool.

The following table is given showing a comparison between the ordinary process of scouring and the electrolytic method:

TESTS PERFORMED ON SAMPLES DRIED UNTIL CONSTANT.

—	Products Weighed.	Raw, in the Grease.	Montevideo Wool Washed in the Ordinary Machine.					Montevideo Wool Washed in the Baudet Electrolytic Machine.				—
			After Ordinary Scouring	After First Washing Vat.	After Second Washing	After Third Washing.	After Fourth Washing.	After First Electrolytic Vat	After Second Electrolytic Vat.	After First Washing Vat.	After Second Washing Vat.	
		Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	
A	Wool fat (suint)	17.655	15.0	16.090	5.540	2.062	1.925	5.410	3.180	1.63[illegible]	1.410	A
B	Suint and soap..	4.325	1.440	1.565	1.610	1.260	1.045	3.925	1.385	1.775	1.475	B
C	Mineral salts and coloring matters soluble in water........	9.925	1.980	1.525	0.940	0.760	0.665	1.870	1.550	1.250	0.485	C
D	Dust...	25.610	30.660	5.505	2.435	1.570	0.915	8.975	5.910	0.890	0.850	D
E	Clean wool ...	42.485	50.920	75.315	89.475	94.350	95.450	70.820	87.975	94.459	95.860	E

The composition of the scouring liquor from the first electrolytic vat was as follows:

sp. gr. before filtration = 10.5° Bé.
sp. gr. after filtration = 11.0° Bé.

Matters in suspension:

Wool fats (suint) = 13.684 grams per liter
Soapy matters, etc. = 3.008 " " "

9. Carbonizing of Scoured Wool.

After wool is scoured it is frequently carbonized before being dried. This is for the purpose of removing all vegetable impurities from the fiber, including threads, plant tissues and burrs. For the purpose of carbonization the scoured and washed wool is steeped for several hours in a dilute solution of sulfuric acid of 5 to 8 Tw., then well squeezed or hydro-extracted and then dried in a carbonizing oven or drying apparatus. It is important that the acidified wool be first dried at 125 to 140° F., and finally carbonized by heating to 212° F.

If the treated wool were heated directly to the higher temperature it would be made harsh and brittle.

After heating the dried wool is put through a machine with fluted rolls and a rapidly revolving toothed cylinder or beater. This mechanical action breaks up all the decomposed vegetable matter and dusts it out of the wool. As the purified wool is still in a rather strongly acid condition it is washed first in warm water, and then in water

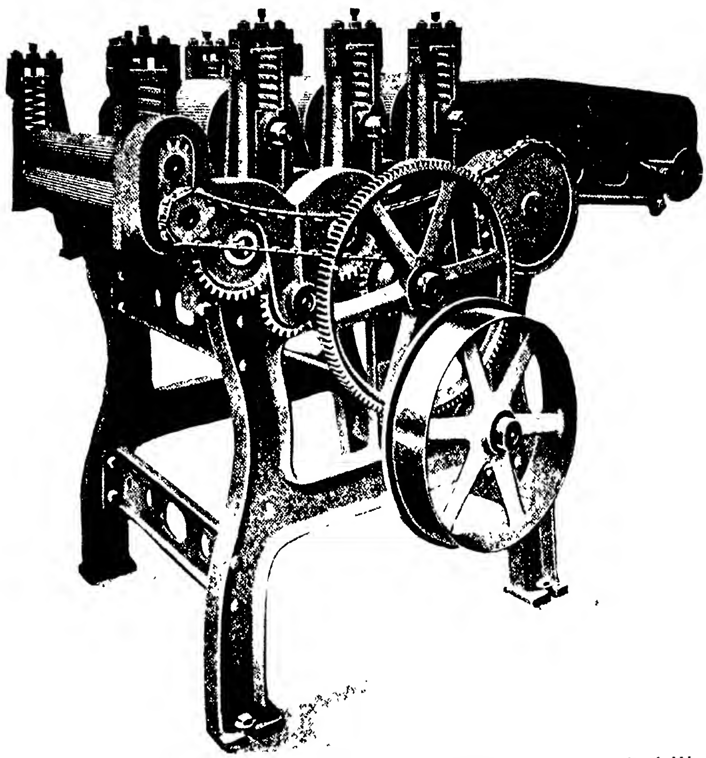

FIG. 27.—Crush Rolls for Pulverizing Vegetable Matter in Carbonized Wool Stock (James Hunter).

containing a small amount of soda ash for the purpose of neutralizing the acid residues, and finally in fresh water so as to eliminate all excess of soda ash. This latter is very important, as if any residue of alkali were left in the wool, on drying it would become concentrated and cause injury to the fiber, and also have a bad effect on any after dyeing process.

Frequently in large establishments the acid treatment is carried out in continuous process in a Leviathan machine, and often the wool is slightly blued during the washing process after carbonizing, so as to give the fiber the effect of being bleached.

Chapter V.

Scouring of Wool (Cont'd).

1. The Drying of Wool.

The proper drying of the wool after scouring is an important process, and one which is liable to be carried out in a careless and haphazard manner. It may be said that air-drying at the ordinary temperature gives the best results; but as this requires a long period of time it is seldom practicable. Drying by means of artificial heat is usually employed, and great care must be taken not to allow the temperature to become too high, or the wool will become "burnt"; it loses its luster, acquires a harsh feel, and becomes brittle and often discolored.[1]

The principles to be borne in mind in the proper drying of wool are the following: In the first place, the more water present in the wool, the higher the temperature to which the fiber may be subjected without danger of injury; for the heat is first used up in volatilizing the water, so that the fiber itself is not really subjected to a higher temperature at all, and, of course, the higher the temperature the more rapid will be the removal of the water. In the second place, as the amount of water in the wool becomes lessened there should be a corresponding decrease in the temperature to avoid overheating of the fiber. In the third place, since the amount of moisture volatilized is not only dependent upon the degree of temperature, but also on the amount of moisture already in the atmosphere surrounding the wool, the rapidity of drying of the wool will be much increased by systematically removing the air as it becomes saturated with moisture and supplying fresh dry air to come into contact with the wool; the greater the supply of air per minute the more rapid will be the volatilization of the water. In the fourth place, it can be readily understood that the wool should not be dried lower than the normal content of moisture, and at this point

[1] Ordinary dry air gives the best results, but it becomes so quickly saturated with moisture that it is not practicable to use it owing to the large volumes required. The common systems of drying wool have arrangements whereby currents of warm air are circulated freely in and around the wool, which is spread out in such a way as to give free access to the currents, which abstract the moisture from it. It must be noted, however, that drying with a high temperature tends to discolor the wool, injure its luster and handle, rob the fiber of its suppleness, and impair its elasticity and strength. It is quite as important to dry the wool carefully and at a low temperature as it is to scour it with the liquor not too strong and the temperature not too high. If wool is injured by too high a temperature in either of these processes, it is much more difficult to work in the subsequent processes, and an inferior product is obtained at every stage, at a greater cost, and with increased production of waste. Wool should not be dried at a higher temperature than 160° F., and the best results are obtained by drying at temperatures ranging from 90° to 120° F. A temperature of 160° F., or even higher, will not injure the wool so long as it is giving off moisture.

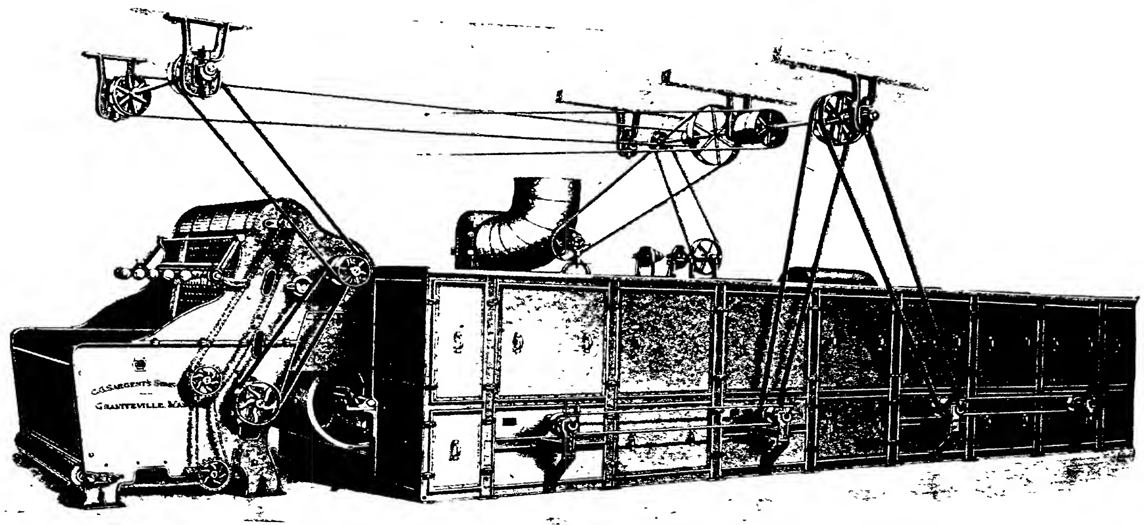

FIG. 28.—Raw Stock Wool Dryer (C. G. Sargent).

the temperature to which the fiber is exposed should be about the normal temperature of the air.

The aim of most drying-machines for wool is to realize these conditions as perfectly as possible, and at the same time to allow of the rapid drying of the wool with the most economical expenditure of heat. In most forms of drying-machines, the wool is carried through a long chamber or series of chambers. As it enters the machine it meets a comparatively high temperature, and care must be had that there is no danger of the wool becoming unevenly heated, with the danger of burning portions of the mass. As the wool progresses through the machine it is continually losing its excess of moisture, and the temperature to which it is subjected is correspondingly lowered. As the

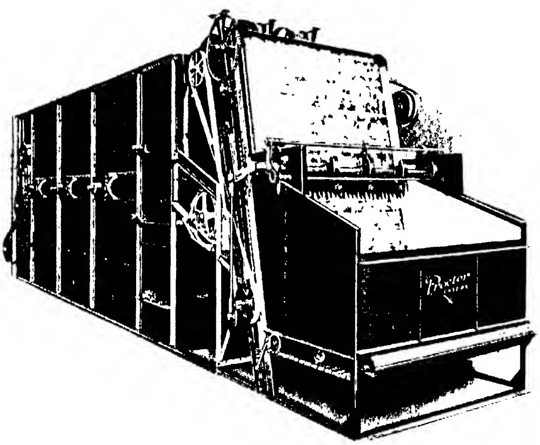

FIG. 29—Apron Dryer (Proctor & Schwartz).

wool finally emerges from the machine the temperature should be not far above that of the air, and the wool should be normally dry. During the progress of the wool through the machine it is met by a current of air blown or drawn through by means of a suitable fan. It is by means of this draught of air that the volatilized moisture is removed from the fiber.

If wool is dried at a temperature of 212° F. until all of its moisture is removed, the fiber will suffer a permanent injury to its physical properties. Even if exposed to temperatures considerably below this until it arrives at a condition in which its hygroscopic moisture is far below that normally present, the fiber will undergo permanent change in its physical properties and will not return to its original state when exposed again to normal conditions of temperature and moisture. A portion of the moisture which is contained in the wool fiber under

normal conditions is held there, no doubt, in a merely mechanical state; that is, absorbed in a capillary manner by the porous nature of the wool; but another portion of such moisture appears to exist in some form of chemical union with the fiber itself. The moisture held by the fiber in this condition may be termed "water of hydration" and its removal no doubt causes certain changes in the intimate composition or structure of the fiber so that its physical properties undergo permanent alteration. Just what amount of this "water of hydration" is normally present in wool has never been determined, but it is no doubt equal to several percentage. The water of hydration of wool may be compared with the water of crystallization of certain salts, such as soda crystals, bluestone, etc. The physical properties of these salts are largely dependent upon their water of crystallization, although their

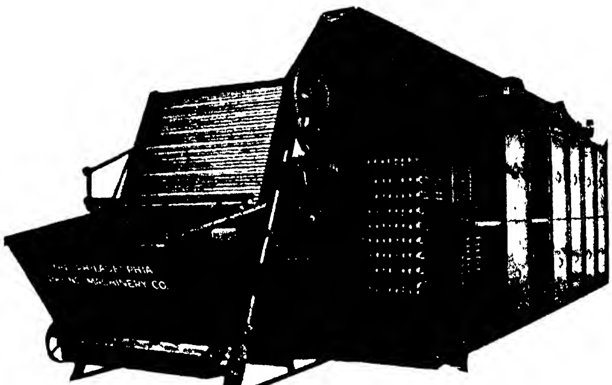

FIG. 30.—Hurricane Dryer for Loose Wool.

chemical nature is in no wise affected by it. For instance, soda crystals occur in the form of large, well-defined crystals, colorless and transparent, hard and brittle. If, however, these crystals are heated above 212° F. for some time so that the water of crystallization is driven off, the crystals lose their physical properties, and change to a white powder, without any crystalline form. In the same manner when crystals of copper sulfate (bluestone) are heated so that they lose their water of crystallization, the crystals lose their blue color and crystalline character, becoming white and pulverulent.

The destructive action of high temperatures on wool may be prevented to a certain extent by the addition of a solution of glycerin to the fiber. It is said that if wool is saturated with a 10 percent solution of glycerin the material may be exposed to a temperature of 280° F. without injury to the fiber. This action can no doubt be explained by the fact that glycerin is a substance which retains water with great power, and that even at such an elevated temperature all of the water

is not removed from the wool fiber, as would otherwise be the case if the glycerin were not present.

2. The Scouring of Yarn.

When wool is carded or combed and spun, it is necessary to add a certain amount of oil to the stock in order that the fibers may not become injured in the mechanical processes through which they pass; the presence of the oil also renders the wool more plastic and hence considerably facilitates the working of it into fine yarns. To woolen yarns, as a rule, a much larger amount of oil is added than to worsted yarns, and the oil is also usually of a different character.

Before the yarn is in a fit condition to be dyed, the oil which has been added must be removed; also the miscellaneous dirt which the

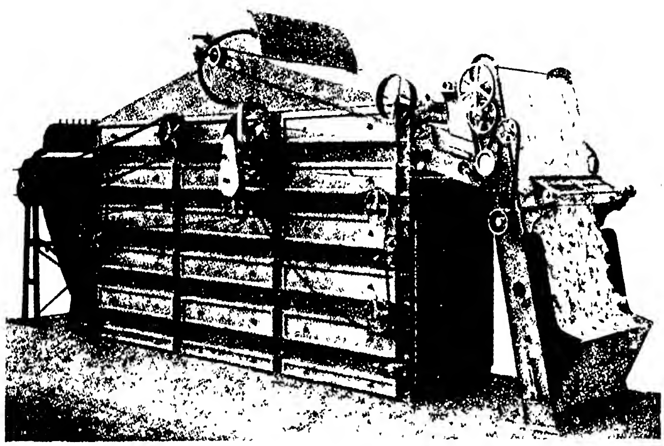

FIG. 31.—Dryer for Loose Wool (English Type).

yarn has collected during the processes of manufacture must be taken off. The amount of impurities to be removed from yarns will of course vary largely with the character of the yarn and the method of its spinning. As a rule, however, woolen yarns will lose from 8 to 15 percent on scouring; worsted yarns will lose only from 2 to 10 percent; carpet yarns may lose as high as 25 percent. In some cases, such as mule-spun worsted yarn on the French system, no oil is used, and the yarns do not require scouring.

The kind of grease and other impurity to be removed from yarn is far different from that to be found in raw wool. It consists chiefly of an easily emulsifiable oil together with ordinary dust collected on the yarn. The process of yarn scouring, however, is very similar to that of scouring raw wool; a soap solution being employed, to which is usually added a certain amount of alkali. For the scouring of raw wool, as a rule, the amount of alkali is in excess of the soap; but for

scouring yarns, the reverse is the case, and more soap than alkali is used. The exact composition of the bath will vary with the character of yarn to be scoured, and the nature of the oil on the fiber; but as a rule, a bath may be used containing from 2 to 4 ozs. of soap and ½ to 2 ozs. of soda ash (or potash) per gallons. The yarn is simply worked in this bath at a temperature of about 140° F. until thoroughly cleansed. For fine single worsted yarns of good luster which are liable to become felted or lose their brilliancy, it is best to use a scouring bath containing only soap, and not have the temperature above 100° F. In some cases, woolen yarns may be very dirty and contain a considerable amount of iron ground in with the grease present. Such yarns, for instance, which are made of the wool which is passed first through a newly ground set of cards. If yarn of this nature is scoured in a bath containing alkali, the iron will be fixed as a mordant in the fiber, and it will be impossible to get the wool white, or to dye it satisfactorily. In order to obviate this trouble the yarn should be scoured in a bath containing only soap in solution, when it will come out white and free from iron.

After the yarn has been sufficiently scoured, it must be well washed, preferably in lukewarm water, in order to remove all traces of the soapy liquor; for if the soap becomes dried into the wool it will give rise to all kinds of difficulties and faults in the after dyeing and finishing operations.

The proper scouring of yarn is a very important process to the dyer; for if the yarn has not been thoroughly cleansed of the impurities it contains, and if the soap, in turn, has not been completely removed by washing, imperfect dyeing will nearly always be the result. The dyer himself should always scour the material he is to dye, unless he can always rely on it having been done previously in a satisfactory manner. Sometimes, yarns are treated with solutions of sodium bisulfite after scouring, in order to give them a whiter appearance. In such cases, more or less sulfur dioxide remains in the wool, and may cause bad and unevendyeing due to the destructive action of the sulfur dioxide on the dyestuff. The practice of sulfuring wool in this manner is to be deprecated, as it becomes an uncertain and injurious factor in the dyeing operation. Its bad effects may be counteracted by subjecting the material to the mild action of some oxidizing agent, such as a weak bath of chloride of lime, sodium peroxide or potassium permanganate. This destroys any residue of sulfur dioxide present and renders it harmless.

In the case of yarns which are hard twisted, there is a tendency to curl up, especially when wet out. Such yarns should be stretched and steamed before scouring in order to remove the curl, otherwise they are liable to become seriously matted and tangled. Yarn stretching depends on the fact that when wool is stretched and steamed or placed in hot water, the fiber becomes very plastic, like a piece of steamed horn; and if it is cooled while still under tension the fiber will retain its straight form, and show but little tendency towards curling when again wetted. This operation is often spoken of as "crabbing" the

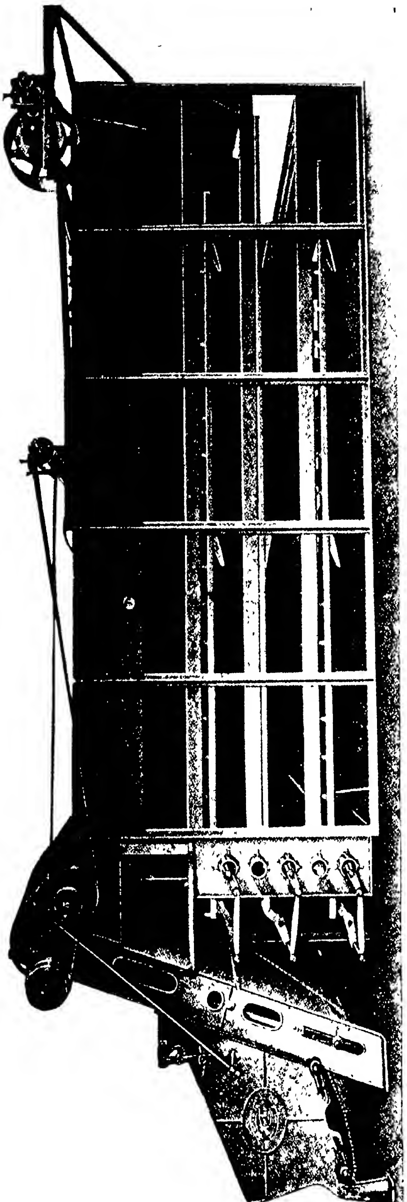

Fig. 32.—Agitating Table Dryer (James Hunter).

yarn; although this term is more often applied to a similar operation on piece goods.

Sometimes yarn is spun from fleece-washed wool in the grease without any previous scouring of the raw material. In such cases, of course, a considerable amount of the original wool-fat is still present in the yarn, and the latter should be scoured in about the same manner as the raw wool itself would be.

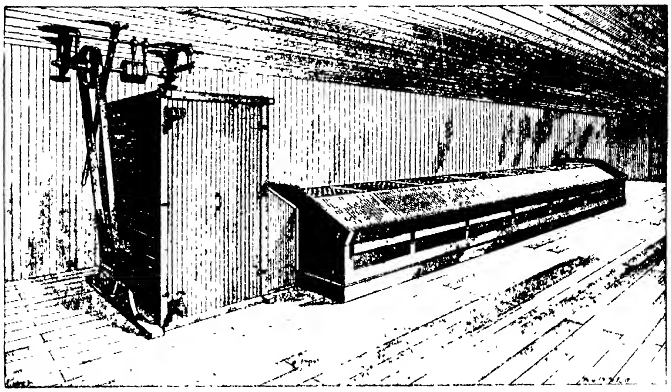

FIG. 33.—Table Dryer for Loose Wool (Proctor & Schwartz).

3. Wool-oils.

It has already been noted that when scoured wool is carded and spun it is necessary to add some oil to the stock in order to get the best results from these operations. The oil is applied in order to lubricate the fibers and make them more pliable; it also has the effect of preserving the quality of the surface serrations on the fiber, as to a certain extent the oil furnishes a protective coating over the entire surface of the fiber. This permits of the wool stock being opened and the fibers properly disentangled in the carding with a minimum of physical damage. Furthermore, if the scouring has been too severe or if the drying has been carried out at too high a temperature or if there has been an improper circulation of air through the drying apparatus, the wool will have been rendered unnecessarily harsh and brittle, and hence the addition of oil is required to counteract this as far as possible. If greater care were exercised in the processes of scouring and drying there would no doubt be less necessity for the oiling of wool stock, or at least, less quantity of oil would be needed.

Oil is usually applied to wool stock in the form of an emulsion, made by mixing the oil with water and alkali. As some oils are more easily emulsified than others, it becomes a question of considerable importance to select the proper oil for treating the stock previous to spinning. For worsteds, it is customary to employ olive oil of good grade, this being emulsified with soap, alkali, ammonium carbonate,

ammonia water, or borax. On lower grades of stock, cheaper oils and preparations are frequently used, and sometimes these are rather difficult to subsequently remove from the fiber by ordinary scouring. Linseed oil is sometimes used in such mixtures, and as this oil undergoes oxidation on exposure to the air and becomes dry, yarns on which it is used should be scoured soon after spinning, otherwise the oil will form a kind of varnish over the fiber, the removal of which will give considerable difficulty. This same observation is also more or less true of such semi-drying oils like cotton-seed oil, etc.

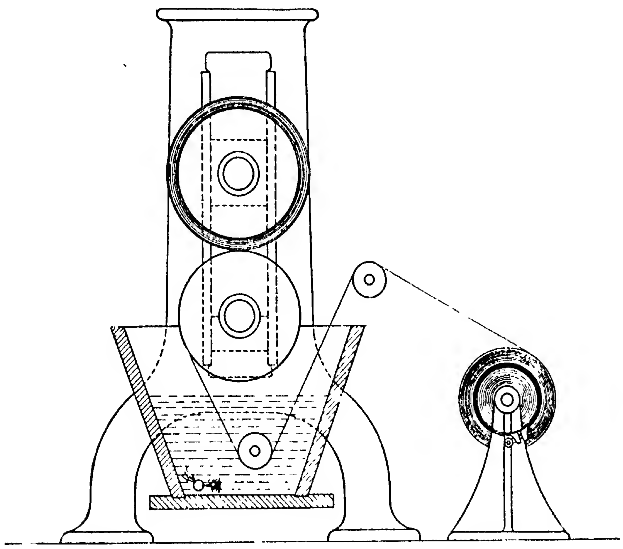

FIG. 34.—Simple Crabbing Machine.

The principal oils employed in practice are the vegetable and animal oils, as these are the most readily emulsified and saponified. The oils that are actually employed are: olive oil, lard oil, olein, cottonseed oil, black oil and brown oil (recovered oils).[2] There are also numerous proprietary compounds and emulsions on the market, usually consisting of an oil and a soap solution and generally having more or less added alkali.

The best oils to employ for wool stock are lard and olive oils, or mixtures of these. They appear to amalgamate satisfactorily with the

[2] Various kinds of recovered oils, and mixtures of recovered oils with vegetable oils are used in large quantities in the medium and low-grade woolen trade. The recovered oils are obtained by reclaiming the fat or grease from the waste scouring liquors of raw wool and the grease resulting from the scouring of yarn and cloth. In the first case the oil is a combination of wool grease and the fatty matters from the soap used in scouring, while in the latter case the oil consists of a mixture of the soap fats and the grease from the oil used in oiling the wool. Recovered oil in its most impure form is termed black oil, and when slightly purified it is known as brown oil, while olein oils are produced by further purification

wool fiber and with the natural oil or grease which may be left in the wool from the scouring of the raw stock. These oils do not harden or gum, and consequently do not clog up the teeth of the card wire. In applying these oils it is customary to use them in the form of an emulsion with water containing borax (or other alkali); generally about

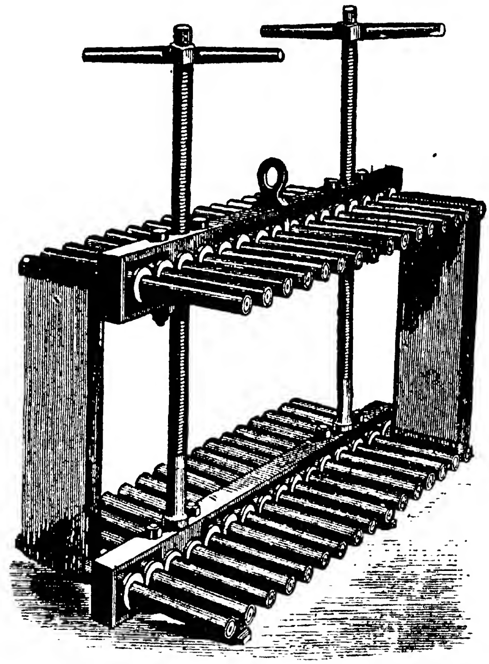

FIG. 35—Yarn Stretcher.

equal parts of oil and water are used, sufficient borax being added to bring the mixture into the state of a good permanent emulsion.[3] The amount of oil emulsion required for wool stock is from two to five quarts per hundred pounds of wool. A good emulsion to use for worsted stock is as follows: Dissolve 12 ozs. olive oil fig soap and 2 ozs. pearl ash in 2 gallons water; then stir in 5 quarts of olive oil, and

[3] Wool-oils are practically always applied in the form of an emulsion, as in this form they are more fluid and can be diffused more thoroughly over the material. There are several methods of making an emulsion, the object always being to obtain an intimate mixture or amalgamation of the oil and water. In order to unite the oil and water satisfactorily, soda ash, borax or ammonia is generally employed,—the first alkali being used with the low-class emulsions and the other two with the better-class. The water employed in preparing these emulsions should be soft and pure, and probably the most satisfactory water for this purpose is condensed steam. In preparing the emulsion the water is first heated and the alkali and the oil added with constant stirring. It is important to use neither too little nor too much ammonia, for in the first case the union of the oil and water will not be sufficiently thorough, and in the second case the emulsion will be too thick.

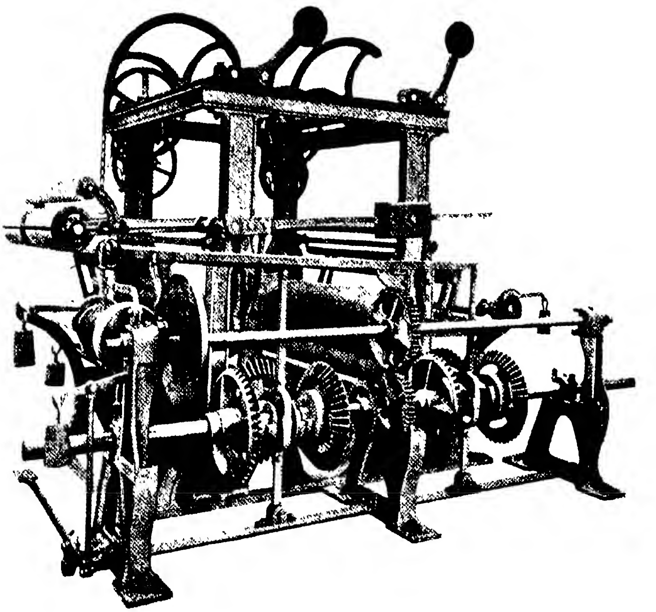

FIG. 36—Double Crabbing Machine.

heat until a homogeneous emulsion is produced.[4] Another form of emulsion for worsted stock is the following: To 2 quarts of water at a

[4] In the preparation of this emulsion it is recommended to cool to 100° F., keep at this temperature for 2 hours, and add after one hour:

Water	50 lbs.
Potassium chloride	25 lbs.

A solution recommended for fine wool is as follows:

Water	200 lbs.
Panama bark	25 lbs.

Stir well at 100° F. and add:

Olive oil	45 lbs.
Ammonia	6 lbs.

If the solution is not white and viscous, add more ammonia and heat the mixture while it is being stirred.

Another emulsion for oiling wool stock is the following:

Water	320 lbs.
Fulling soap	42 lbs.
Olive oil	75 lbs.
Ammonium sulfate	1¼ lbs.
Cottonseed oil	90 lbs.

Heat for 3 hours to 110° F.

Solution for colored tops; mix lukewarm with stirring:

Cottonseed oil	36 lbs.
Black soap	21 lbs.
Water	125 lbs.

Add at a boil:

Irish moss	15 lbs.
Water	100 lbs.

Stir well and allow to cool to 100° F.

Kattenbusch solution:

Potato starch	1½ lbs.
Olein	5 lbs.

Mix into a paste form and add:

Water	58 lbs.

Let boil and stir well.

Labarthe mixture: This has for a base rosin oil mixed with an equal quantity of a gelatinous emulsion of lichen or seaweed. It is claimed that wool-oil with this mixture can be scoured clean in water at 100° F., containing 1 percent of white soap.

temperature of 120° F. slowly add 1 quart of good olive oil with constant stirring; then add 1 gill of ammonia water and stir well; this gives a good emulsion which is very permanent.[5]

From a series of experiments by Spennrath [6] it has been shown that oils employed for wool spinning may be mixed with 30 percent of

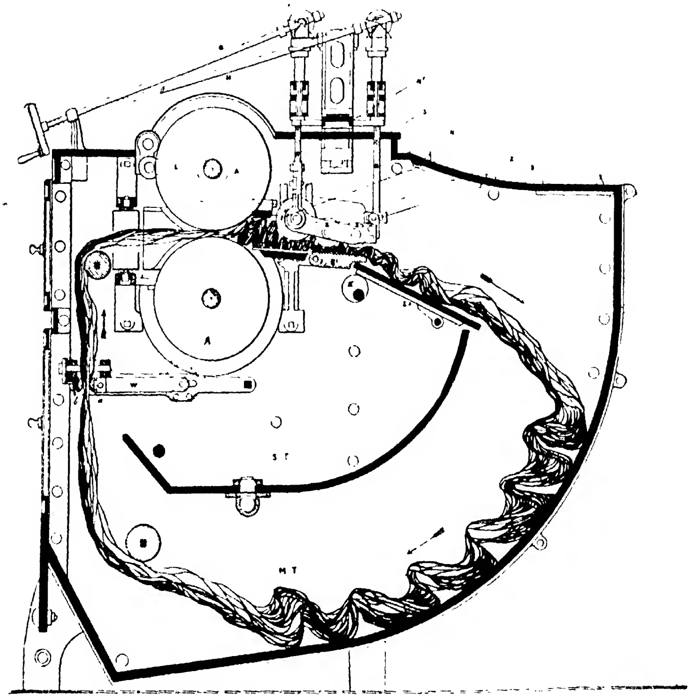

FIG. 37.—Fulling Machine (Crosset & Batisse).

mineral oil without detriment. Though the use of mineral oil cannot well be justified, as it is rather difficult to remove from the fiber, it appears that when mixed with vegetable oils it is easily emulsified by means of soap and soda solutions. If olein is used, a two percent solution of soda is the best scouring medium; whereas if olive oil is

[5] The quantity of emulsion to be employed for oiling wool depends very largely on the kind and condition of the materials composing the blend of stock. For a high-class all-wool blend about one gallon of olive oil emulsion should be used per 100 pounds of stock. In the case of shoddy or mungo blend the materials will have been pulled in oil and from one to two gallons of black oil per 100 pounds will have been applied prior to pulling, therefore in the blending only about half a gallon of black or brown oil per 100 pounds need be employed.

[6] *Dingler's Polytech. Jour.*, vol. 294, p. 44.

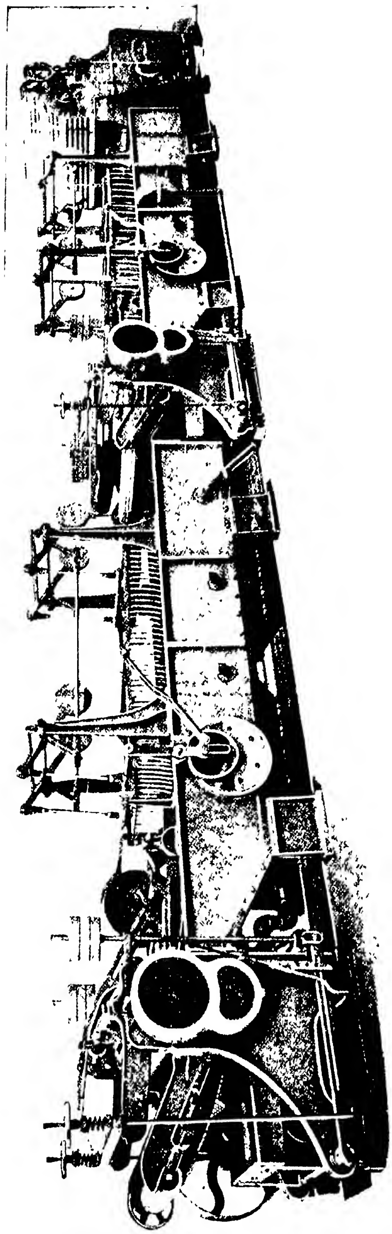

FIG. 38.—Leviathan Scouring Machine (C. G. Sargent).

employed, soap should also be added. Scouring such mixtures with fuller's earth or with ammonium carbonate is not satisfactory. Other authorities, however, discountenance the use of mineral oils for such purposes altogether.

Wool-oils may frequently contain glycerin, soap, and other constituents. A patented product, for instance, called Soluble Neolin, is composed of 100 parts water, 15 parts soap, 30 parts heavy petroleum oil, 8 parts potassium carbonate, and 25 parts glycerin.

The use of wool-fat itself has been suggested as a wool-oil. This substance has the good property of very readily forming an emulsion with warm water alone, and also with soap or alkaline solutions; also it does not harden or otherwise suffer alteration on exposure; nor does it become rancid or in any manner injure the good qualities of the wool fiber. Emulsions of this material have appeared on the market and seem to have met with considerable favor. Such an emulsion may be formed by dissolving one part of soap and five parts of wool-fat

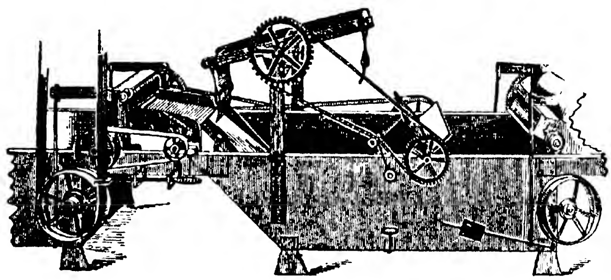

FIG. 39.—Scouring Machine, Old Paddle Type.

in six parts of hot water, stirring the mixture until a thick creamy emulsion is formed, after which about 90 parts of cold water are added. This emulsion is of a very stable character, and remains homogeneous and permanent even when cold.

Wool stock should be oiled just as the material is passing into the cards, for the addition of the oil does not only give proper lubrication to the fiber, but the water which is also present in the emulsion adds much to increasing the plastic quality of the wool and thus aids in its proper working. If the emulsion is applied too long before the wool is put through the card, the majority of the water in the emulsion will evaporate, thus causing the wool to become drier than it should be; and also as the water evaporates the oil of the emulsion is liable to separate out unevenly throughout the stock, and thus give rise to uneven results in the spinning operations.

An ideal wool-oil should possess considerable fluidity so as not to gum up in the cards, and also to enable the oil to spread in such a manner as to obtain as thorough and even a distribution over the wool as possible, and at the same time it must also possess sufficient

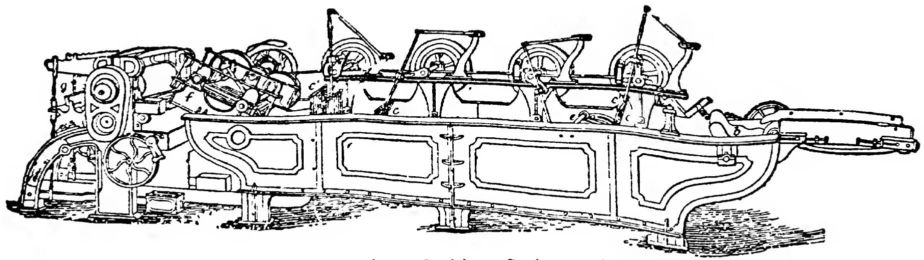

FIG. 40.—Scouring Machine, Swing Rake Type.

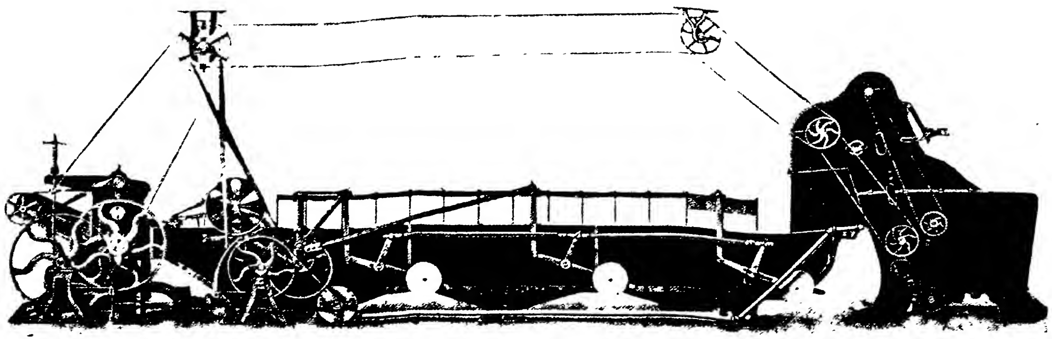

FIG. 41.—Scouring Machine, Rake Type (C. G. Sargent).

body and viscosity in order to remain on the fiber. It should not be oxidizable, nor possess any oxidizable constituents. Furthermore, it should be completely emulsifiable in order that it may be easily and completely removed by simply scouring; it must be non-evaporative, otherwise the wool would become harsh and brittle before the spinning was completely finished, and also different lots of wool would not show even results; it must be free from sulfuric acid, or, in fact, from acid of any description, else the metal of the cards and spinning machines would be attacked and rusted, and considerable iron would get into the yarn; it should not contain any substances which favor the growth of fungi or other micro-organisms or ferments, as these will weaken the wool fiber; in the opinion of many, it should be free from all hydrocarbon or mineral oils; and finally it must also be cheap.

From the experiments carried out by Spennrath[7] on the use of mineral oils for wool have developed some interesting facts. In the case of goods treated with mineral oil solely, the best results in washing were obtained with a fulling soap, and the least good with soda ash; fuller's earth did not work at all satisfactorily. When a mixture of equal parts of mineral oil and olein were used, the best washing medium proved to be soda and soap; fuller's earth did not answer, and ammonium carbonate was found to be absolutely useless, as it led to the precipitation of a sticky mass which adhered to the fibers. When a mixture of olive and mineral oils was used, soap proved to be the most efficient scouring agent, while ammonia was not at all satisfactory. From his experiments, Spennrath concludes that mineral oil may be used to the extent of 30 percent in the preparation of wool-oils. Walther, another experimenter, on the other hand, concludes that mineral oils should be entirely excluded from wool-oils. Lewkowitsch[8] supports the opinion of the latter, and claims that mineral oil should not be used in connection with better class goods.

It is claimed in England that when everything is taken into consideration, olein is perhaps the most satisfactory material for the oiling of woolen goods; but in the case of worsted material,[9] olive oil alone should be used, as this is the only oil which will allow the rovings to remain for any length of time without oxidizing. When olein is used on worsted, it is impossible to spin within 8 or 10 counts to that which can be spun when olive oil is used.

All authorities are agreed that the best oil to fulfill the required conditions is a good quality of olive oil. A good test for the quality of olive oil for use on wool stock consists in mixing three parts of the oil with one part of concentrated nitric acid, and observing the color after standing for 1½ hours. If the oil is pure, or only mixed with lard or castor oil, the color will be yellowish; but if seed oils or sperm, seal, whale, or mineral oils be present, a red color will have developed, varying in intensity with the amount of other oil present. Seed and

[7] *Dingler's Polytech. Jour.*, vol. 294, p. 44.
[8] *Jour. Soc. Dyers & Col.*, 1896, p. 60.
[9] Although there is no fixed standard for the amount of oil to be used on worsted tops, it has been found that from 2 to 3 parts of oil per 100 parts of tops is about the best average.

seal oils give a reddish orange color, while mineral and fish oils give a darker red. The addition of lard and castor oils to olive oil increases both its density and its viscosity. Nearly all oils are somewhat volatile, but olive oil is very slightly so, while with sperm and mineral oils the evaporation is considerable.

It is poor policy to employ an unnecessarily cheap oil on wool stock; though there is frequently a tendency to use a lower-class oil than the material warrants, and this is especially the case where yarns

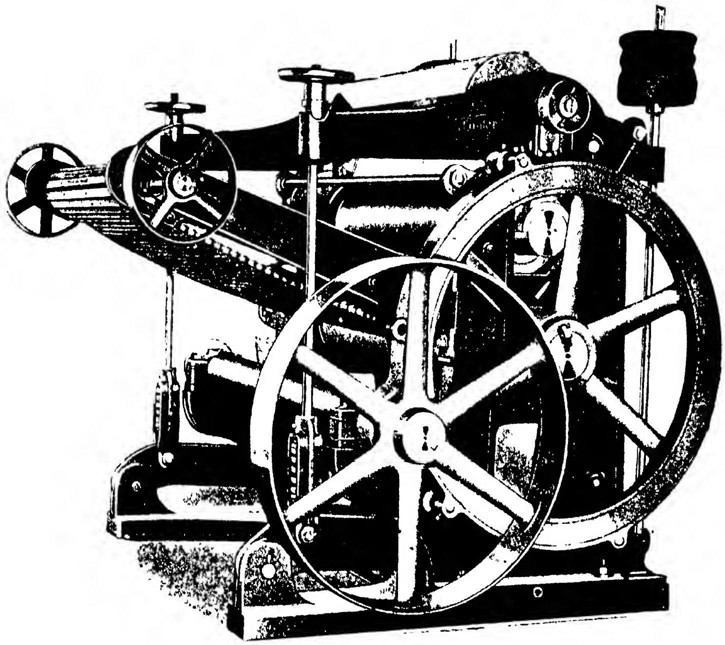

FIG. 42.—Delivery End with Squeeze Rolls and Apron (C. G. Sargent).

are being spun for sale in the scoured condition.[10] Whereas the first cost of the oil is an important matter and must be adjusted to economically suit the grade of material being manufactured, nevertheless there are certain disadvantages in the use of very cheap oil which should be thoroughly understood, for a low-grade oil may adversely affect the production of the yarn both as regards to quality and quantity. It oftens happens that in cheap oils a considerable quantity of

[10] If yarn is to be scoured immediately after spinning and then dyed or sold it is general practice to employ a lower class of oil than when the yarn has to be stored for some time or even if it is used directly for weaving in the unscoured gray condition. It is easy to appreciate the reason for this practice, for an inferior oil oxidizes much more rapidly than a higher grade oil, and a sticky resinous deposit is formed on the fibers which is very difficult to remove or scour from the material, and the longer the material is kept in the greasy condition in the form of either yarn or cloth, the greater is the degree to which oxidation may proceed.

free acid is present; this is especially true with black recovered oil where an excess of sulfuric acid has been employed in the "cracking" of the waste scouring liquor from which this oil is derived, and even in the case of olein oil, residual acid may be left in the oil through improper manufacture. The presence of this acid in the oil materially shortens the life of the card clothing and the increased cost of this item may far overbalance a supposed saving in the original cost price of the oil.

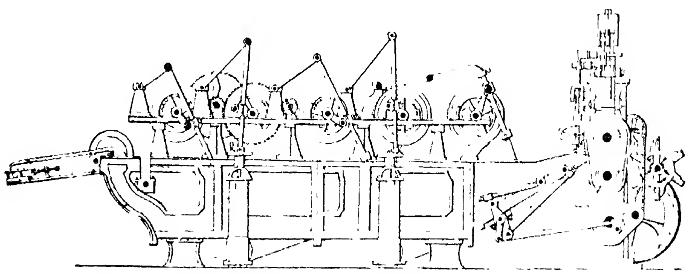

FIG. 43.—Swing Rake Scouring Machine (English Type).

4. The Scouring of Cloth.

Before woven cloth can be put through its finishing operations proper, it is necessary that it be scoured in order to remove from it the grease and dirt which it contains. Sometimes yarn is woven direct into a fabric without being scoured; this occurs in the case of yarn in

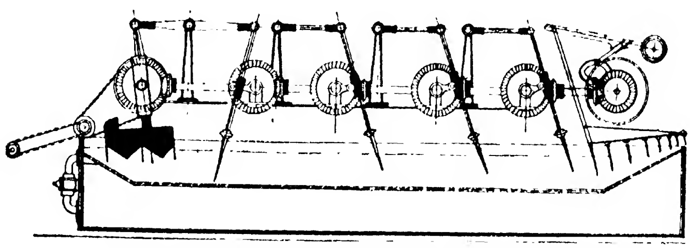

FIG. 44.—Section of Swing Rake Scouring Machine.

the gray, or with colored yarns spun from stock-dyed wool. In such cases, of course, the same impurities are present in the cloth as would be found in the yarn, together with any sizing material, etc., which may have been used in addition. Also, the cloth in the process of weaving and handling acquires a certain amount of additional dirt and foreign matter beyond even that which is to be found in yarns. On the whole, however, the impurities in cloth may be taken as being of about the same class as those in yarn, and are to be dealt with in the same manner; the chief difference being in the manipulation

of the material and the form of apparatus employed for the scouring.

In the case of cloth containing dyed material, especially if yarn dyed, it is essential that the scouring be conducted in such a manner as to least injure the color; though it may seem from this very circumstance that the dyes employed for the coloring of loose stock should be of a class that is fast to rather severe scouring; for this loose stock is spun up into yarn with the addition of oil, and is not scoured until after the piece has been woven; in consequence of which, if the dyes are not fast to scouring, the color will run and stain the goods. If the wool is dyed in the form of yarn, this has previously been scoured before dyeing, hence in the woven piece there will be but little grease, and the scouring need be but very mild. On this account, yarn-dyed material, as a rule, need not be dyed with as fast colors as loose wool. If, however, dyed yarns are woven with gray

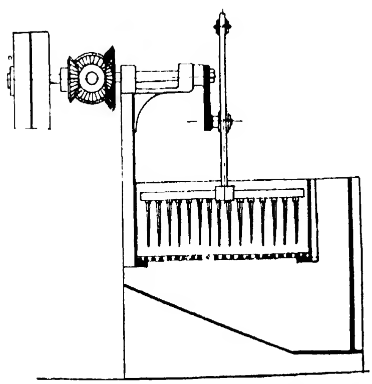

FIG. 45.—Cross-view of Swing Rake Scourer.

yarns, or with yarns from loose stock dyed material, the same conditions will apply as if the entire piece were made from stock-dyed wool, and all the colors would have to be fast, as the scouring would have to be about as severe as if the piece did not contain yarn-dyed wool, but only stock-dyed wool. From these remarks it may be easily understood that the proper scouring of woven pieces will in a great measure be regulated by the character of the goods, and the scouring baths will be weak or strong, neutral or alkaline, according to the condition in which the yarns exist in the piece and the character of the dyes employed.

Many pieces woven from mixed yarns of cotton and wool (known as *union* goods) shows a tendency to crimp and cockle up when scoured. This is due to the unequal shrinking of the two yarns. The same condition will also exist to a greater or less extent in pieces woven from yarns made of different classes of wool. In order to overcome this difficulty, the pieces must be subjected to a process analogous to that of yarn stretching, and known by the name of

crabbing. The cloth is passed in a stretched condition through hot water and then allowed to cool while still stretched. Steaming may also be resorted to, in which case the material is wound around a perforated cylinder through which steam is forced.

It is said that in the case of certain oils being used for oiling the wool, crabbing by steam causes an oxidation of the oil, producing decomposition products which are usually colored and are of a resinous character and difficult to remove. This may sometimes account for the appearance of stains, the origin of which is otherwise unknown.

When woolen pieces are scoured with soap, unless they are subsequently washed well with warm water, there is danger of some of the soap being left in the cloth, with the result that uneven results will be obtained in dyeing. Coarse, common goods can usually be scoured for dyeing both quicker and cheaper by the use of alkali than by the use of soap. Worsted material, however, should be sparingly treated with soda ash, or even with potash, as the effect upon the handle of the goods becomes very marked; even the use of a soda soap tends to make them somewhat harsh. Fine woolen material containing chiefly olein oil with a large proportion of fatty acid, may be treated with a much larger percentage of alkali (preferably potash) than goods in which olive oil free from fatty acids has been used, for while the former is readily saponified, even in tepid water, the latter must be removed by the formation of an emulsion.

With the scouring of woolen cloth, there must also be frequently considered the fulling of the same, as the two operations are generally carried out together. But as fulling belongs to the province of cloth finishing, it will not be discussed at this point, beyond giving the following brief remarks. One of the chief points to consider in this connection is that of the soaps to be used; that is, their dirt-removing power and their lathering power. For a good scouring soap is not generally a good fulling soap, an olive oil or olein soap will remain in solution undecomposed at a much lower temperature than a tallow or palm oil soap, and therefore is more readily removed from the cloth by washing. In fulling, however, it is required that the soap stay in the goods for some time, and therefore a tallow or palm oil soap is preferable. But after the fulling operation is completed, these latter soaps require that the water used in washing out the suds be much warmer than with the before-mentioned soaps, in order to secure their perfect removal from the interior of the closely felted fabric.

Chapter VI.

Machinery for Wool Scouring.

1. Machinery for Scouring Raw Wool.

Raw wool was formerly scoured more or less by hand by simply steeping it in the scouring liquors contained in large tanks, usually of a round bowl-like form. The wool was moved about by long poles until thoroughly cleansed; it was then caught up in nets or suitable cages and allowed to drain, then removed to the washing-tank where the poleing was repeated. This method of scouring is still employed in small establishments, but where large production is desired, machines of suitable construction are now almost entirely employed. There are many forms of these machines on the market, with their several points of advantage. In principle, they consist, for the most part, of a long tank, or a series of tanks, containing the scouring solution, and there are usually from three to four of such tanks, or even more if the occasion demands. The long range of machines of this character is usually termed a *Leviathan*. The greasy wool is introduced in the first tank or "bowl," as it is called, by means of a traveling apron, and it is carried along through the apparatus by means of movable forks which maintain the wool in a constant and slow motion. In some cases, the first bowl is filled merely with warm water, which serves to thoroughly wet out the fiber and also to remove the majority of the mechanically adhering dirt. All of the tanks are provided with false bottoms under which the precipitated dirt may settle. In other cases, especially where only three bowls are used, the first one contains the old or dirty soap liquor, while the second bowl contains the clean and fresh soap liquor. The wool passes from the first bowl through squeeze rollers into the second bowl in a partially scoured and comparatively clean condition. It traverses the second scouring bowl, in which all of the grease should be removed, and going through squeeze rollers again, is brought into the third bowl. This is filled with warm water, and is for the purpose of washing the wool free from all soapy liquor. It finally emerges through squeeze rollers and is carried by a traveling apron into the dryer, through which it is carried by a slow motion in such a manner that when it finally emerges it is properly dried. In most mills the dry wool is blown by an air-blast through large pipes from the dryer up to the carding room. When several scouring-baths are employed, they should be so arranged that the dirty wool should first encounter the oldest and dirtiest soap liquor, and as the wool progresses it should meet fresher and cleaner liquors. When the first scouring-bath becomes too dirty

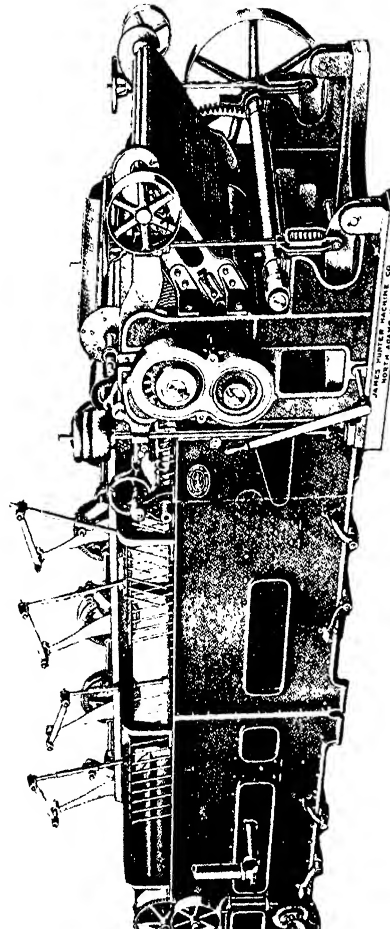

FIG. 46.—Scouring Machine of Fork Type (James Hunter).

to be of further use, it is run off, and the liquor from the second tank takes its place, and so through the series, while in the last scouring-tank a freshly prepared soap liquor is added. The motion of the wool should be so adjusted that the grease is completely removed within the time of scouring, and also with a view not to felt or

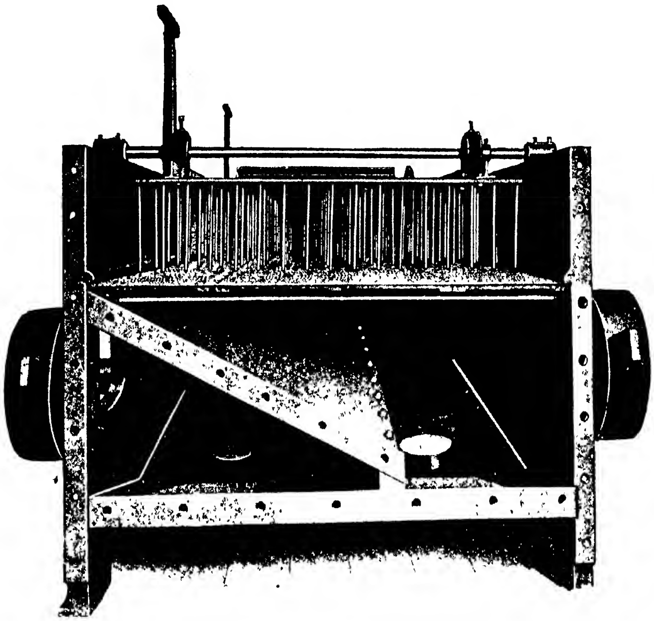

FIG. 47.—Cross-section of Scouring Bowl (James Hunter).

mat the fibers. If the wool is agitated too much felting will take place very rapidly, especially in soapy liquors, and felting will, of course, result in broken and short-stapled fibers in the combing and carding processes, and a consequent loss of value on the wool.[1]

In figure 43 is shown a scouring machine known as the *swing-rake* type.[2] As at present generally used the machine consists of as many

[1] Machines of this character are capable of scouring a large amount of wool per day, and as the material is very gently moved around the fibers are but slightly felted. The repeated heavy compression of the wool by passing through the squeeze rolls is also essential, not only for the obvious purpose of squeezing out the excess of dirty liquor from the preceding tank, but even more for the purpose of breaking up lumps of grease and dirt that would otherwise not be readily emulsified and removed by the scouring liquors. In scouring by this process care must be had not to have too much wool in the tank, as the material should be freely suspended in the liquor so that the soap solution may act efficiently, and also to allow of the dirt and sand to separate out and settle down free from the fiber. The strength of the soap and alkali solution is greatest in the first tank and weakest in the third tank, while the temperature in the first tank should be 105° F., that in the second tank 90° F., and that in the third tank 80° F.

[2] The swing-rake scourer represents the original method of propelling wool through the scour liquor by mechanical means. It has been subjected to many improvements in detail since the original machine was put on the market, and has still a very prominent place

as thirty rakes divided up into three or four bowls. The speed at which the rakes run is usually 6 to 14 strokes per minute, and a higher speed is not desirable as too much agitation of the wool causes it to become felted or matted. The wool enters the machine on the feed lattice, and is caught by the brass-covered immerser which forces it down into the liquor, effectually soaking it, and thus preventing it from floating. On leaving the immerser the wool is caught by the first rake which carries it along through the liquor and delivers it

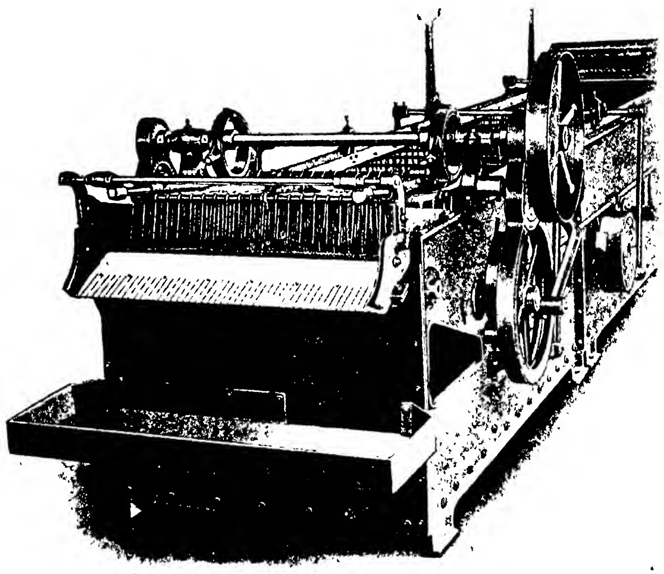

FIG. 48.—Delivery End of Bowl with Auxiliary Rake (James Hunter).

to the next rake, and so on till it reaches the delivery end of the bowl. Each rake is separately balanced and its fitted with brass prongs, and has a slow forward and a quick return movement. As the wool is carried forward through the scouring liquor a large quantity of dirt is removed, and this falls down through the perforated false bottom plates, and as there is no agitation of the liquor below these plates the dirt soon settles to the bottom. The bottom plates are hopper shaped, so that when the outlet valves are opened the mud is washed clear away. When the wool reaches the delivery end of the bowl it is brought on to the lifter and delivered to the press rollers.

in the trade for dealing with the longer, stronger, thicker-fibered wools of the non-felting variety.

The action of the swing rake does not commend itself to dealing with the shorter, finer varieties of felting wools of the merino type, owing to the "piling" action which takes place when the wool is raked forward. This tends to make fine wool become matted and stringy whilst under the action of a hot scouring solution. (See *Text Mfr.*, 1921, p. 44.)

The squeezing press is of strong construction and very heavy, the bottom roller being either of cast iron or steel, and the top roll either of iron wrapped with rope or cloth, or of compressed cloth. In the second and following bowls in place of the rotary immerser there is fitted a rake immerser hanging in the liquor, and balanced so as to allow the forks of the first rake to draw the wool beneath it,

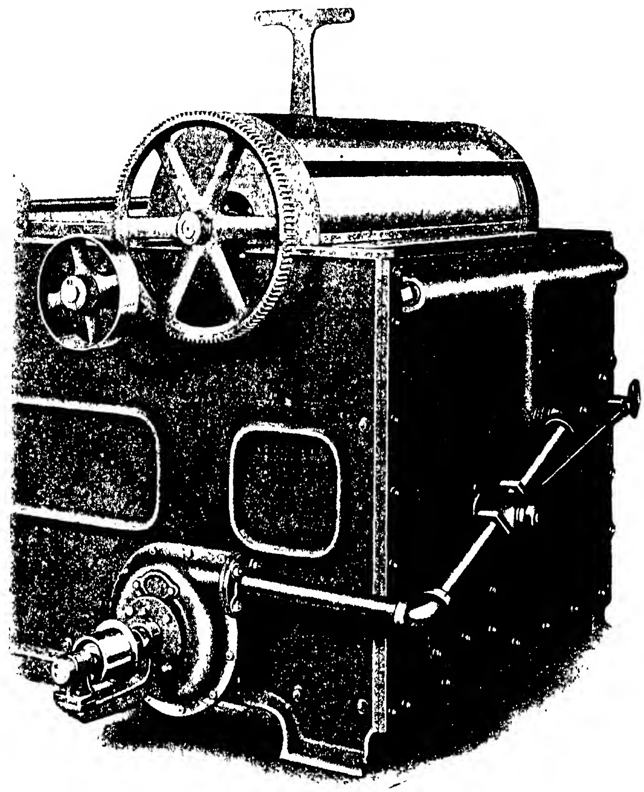

FIG. 49.—Feed End of Bowl with Ducker and Pump (James Hunter).

and so become immersed in the liquor. When the wool being scoured contains much grease and dirt, it is desirable to have the first bowl fitted with a side settling tank into which the water expressed from the wool by the squeezing rollers is led. The water at this point is heavily charged with dirt which settles in the settling tank instead of returning to the main tank. The settling tank also does good service in preventing the scum which rises to the top of the liquor from returning to the bowl. It is advisable to have

three or four bowls in series, as then it is possible to vary both the temperatures and strengths of the scouring baths. Satisfactory scouring liquors for the three bowls are as follows: 1st, six gallons of potash soap with a small quantity of potassium carbonate (pearl ash); 2nd, half this amount; 3rd, pure warm water. The temperatures should be approximately: 1st bowl, 120° F.; 2nd bowl, 100° F.; 3rd bowl, 90° F. It is bad policy to run the wool from a warm scour into cold water, as this quick change of temperature has a tendency to set any grease or sediment which may be on the surface of the fiber.

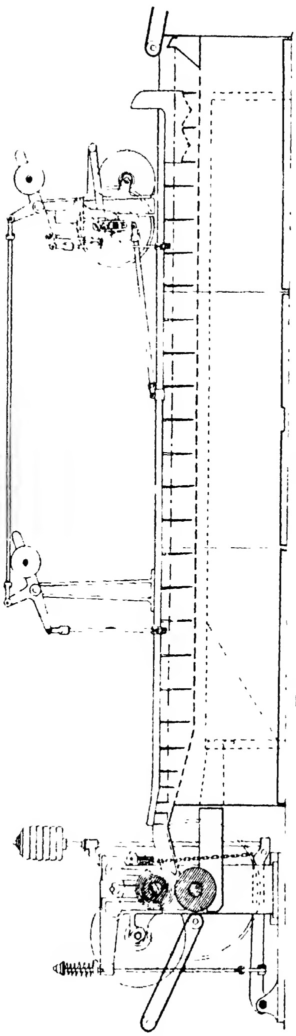

Fig. 50.—McNaught Scouring Machine.

Another type of wool-scouring machine is shown in figure 50, the fork arrangement for conveying the wool through the soap liquor being different in its construction. In this machine the wool passes in a very quiet and gentle manner through the bath. The wool is fed into the machine on a lattice which carries it forward to the bowl. This is divided into several compartments, each provided with a conical bottom chamber covered with a perforated false bottom. The dirt and sand resulting from the scouring pass through the perforated plates into the lower troughs from which they are readily drained away through suitable valves. The forks are all fixed to one complete framework, and all act together, moving forward slowly and then backward quickly. The slow gentle action of the forks is very good for fine short wools, as the motion does not agitate the liquor, and hence prevents undue felting of the fibers. The suds squeezed out at the squeeze rollers at the delivery end of the machine are collected in a tank and return to the last settling trough in the machine. The framework and forks are worked by an eccentric and in such a manner that the forks are carried slowly for-

ward in the liquor, then lifted clear of the solution; the forks next move backward quickly and then are lowered again into the liquor. The framework is balanced by three sets of weights and levers which assist in making the swinging action of the works as gentle as possible. Similar machines are shown in figures 41 and 47.

An English type of wool-scouring machine (McNaught) is shown in the diagram of figure 53. In operation the wool is fed into the machine by the feed lattice and as it drops into the washing liquor contained in the upper bowl, it is immersed by the immerser. The immerser is a necessity, otherwise some of the wool would float on the surface of the liquor and pass from the machine without having been thoroughly saturated. Consequently, at the feed end of each machine an immerser, which is in the form of a brass or copper box with a perforated plate at the bottom, is fastened to the framework of the forks, and moves with them. Since the bottom plate of the immerser is perforated, as it descends into the liquor the latter rushes into the

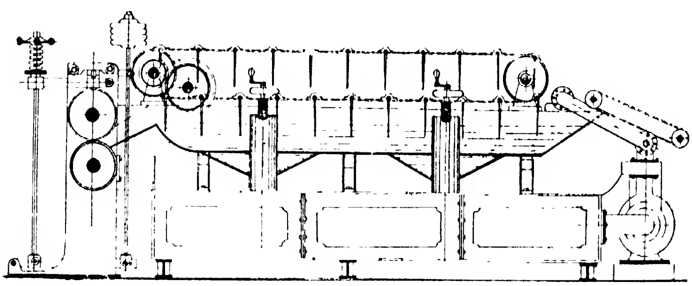

FIG. 51.—Chain Harrow Scouring Machine.

box and thus prevents any considerable displacement, which has the effect of keeping the liquor as still as possible. When the immerser is raised, the liquor rushes out through the perforations on to the wool, and by so doing assists scouring. The wool after being immersed in the liquor is carried forward by the forks, which are given a slow forward movement when in the liquor. The material by the action of the forks is moved slowly forward through the machine until it is moved into the nip of a pair of strong and heavy squeeze rollers, which squeeze out a very large percentage of the liquor, after which the wool is carried by a lattice from the machine.

Referring to the arrangement of the bowls and settling tanks, the bowl in which washing actually takes place is 18 to 24 in. wide and 8 to 9 in. deep, and is connected with the larger bowl in which it is placed by perforated plates that form the bottom. The liquor in the larger bowl is comparatively still, and consequently any heavy sediment can pass through the perforations and settle to the bottom. The bottoms of both the large bowl and settling tank are made sloping so that the sediment will slide down into a channel from which

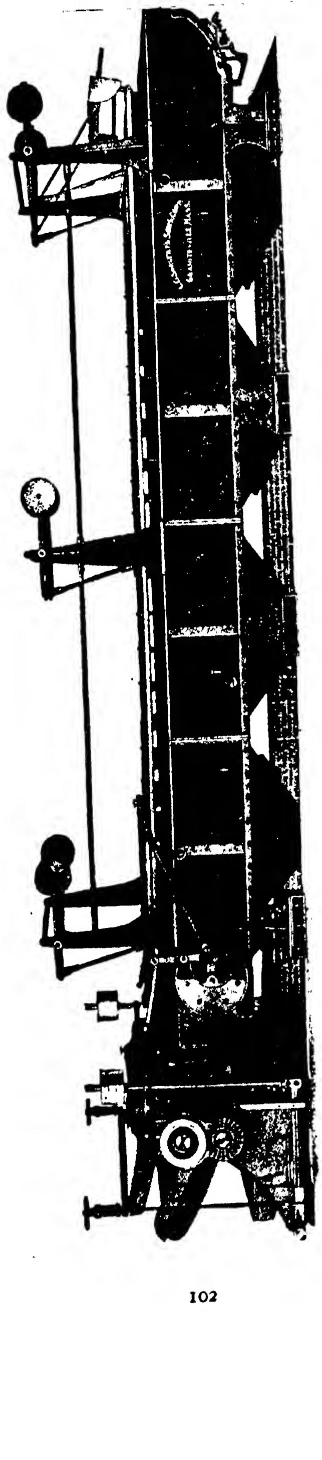

FIG. 52.—Scouring Machine with Reciprocal Motion.

it can be flushed out as desired through suitable openings. Formerly, the excess dirty liquor which was squeezed out by the squeeze rollers was allowed to run back through the material into the washing bowl, and as this is the dirtiest water, since squeezing removes large quantities of dirt, such a method was very objectionable. In this machine, as in all modern machines, the liquor from the squeeze rollers passes through the faller and side plates which are perforated, into a trough. From the trough it runs into the settling tank, in which the heavy dirt settles to the bottom and the scum rises to the top. To facilitate the settling, one or two perforated baffle plates are placed across the tank to break up currents which form due to the flow of liquor. The liquor in the settling tank is pumped back into the washing bowl from the opposite end to that at which it enters,

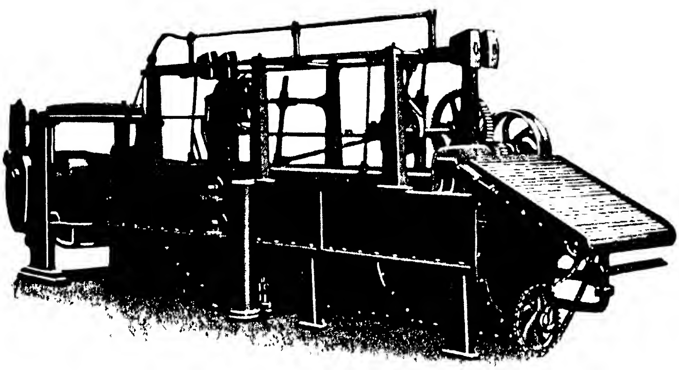

FIG. 53.—Petrie or McNaught Scouring Machine.

and is usually heated before it is sprayed on the wool which is entering the bowl. The liquor in the settling tank is cleanest at about the middle of its depth, and it is from this point that it is pumped. At least one vertical waste pipe is provided, by means of which the liquor is kept at a proper level, and by adding an excess of liquor the scum can be flushed off.

In the older type of rake machines the forks brought the wool close up to the nip of the squeeze rollers; in fact, the forks may be said practically to have lifted the wool into the nip of the rollers. In the best machines, the forks in moving forward deliver the wool to the ridge formed by the bottom of the bowl at the end nearest the squeeze rollers and the perforated plates or grid which slopes down to the nip of the squeeze rollers. As there is liquor passed into the top bowl at the feed end, there is an overflow at the delivery end, as the bowls are set slightly lower at that end. This overflow, which also rids the water in the washing bowl of most of the scum, in conjunction with the movement of the forks causes the wool to be delivered to

the squeeze rollers, and as the wool slides down the slope a quantity of liquor passes from it through the perforated plates or grid.

The fork motion consists of a series of cross-bars which are about 10 in. apart, and which are connected by two light tubular bars that

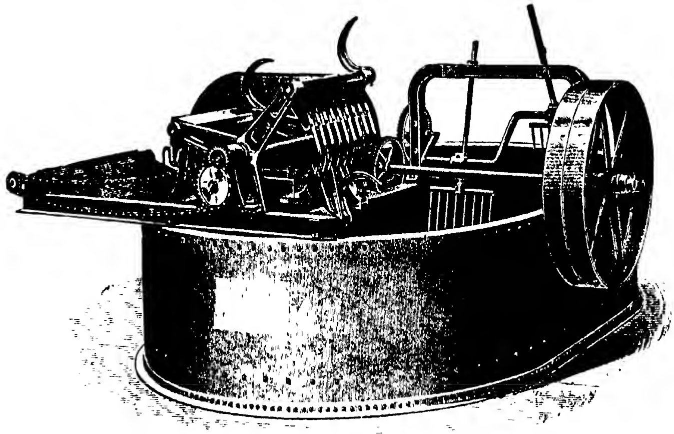

FIG. 54.—Oval Type of Wool Scouring Machine.

extend the length of the bowl. To the cross-bars brass prongs are ixed, and those which are required to work up the incline near the squeeze rollers are shorter than the others. The light tubular bars are

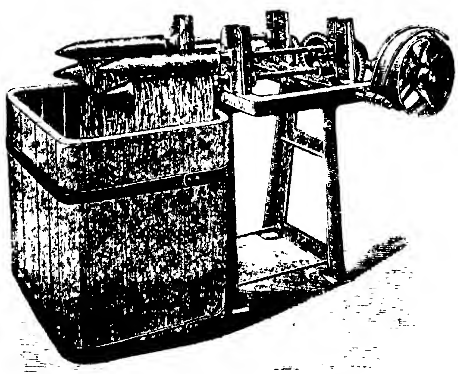

FIG. 55.—Yarn Scouring Machine

attached to connecting rods, and the opposite ends of these rods are in turn attached to levers. A vertical up-and-down motion is given to the forks through these levers by means of a cam, which is fixed to the cam shaft. The cam shaft receives its motion from the

fast pulley by means of gear wheels, which are indicated by double lines. The cam is always in contact with a friction bowl on the end of the lever, which is pivoted to the framework of the machine at its other extremity due to the weight of the forks and framework, the weight of which is almost balanced by the balance weights. To that end of the lever near the friction roller, a rod is connected which is also connected to one of the levers. Consequently, as the cam revolves an oscillating motion is given to the lever. To the top arm of this lever is attached a connecting rod, which conveys motion to the other end of the machine so that both ends of the fork framework are moved at the same time and in an exactly similar manner. A horizontal motion is being given to the forks at the same time as the vertical motion by means of the connecting rod, one end of which is suitably attached to the framework of the forks, while the other end is pivoted to the slotted lever, which swings on a stud that is fixed to the framework. Motion is given to the lever and

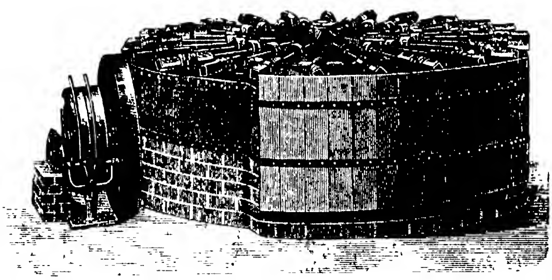

FIG. 56. Circular Scouring Machine for Yarn in Skeins.

connecting rod by a crank fixed on the end of the cam shaft, and which carries an antifriction roller that engages with a suitable slot, consequently, as the crank revolves, the friction roller causes the lever to swing backwards and forwards on its centre, and to communicate a horizontal backward-and-forward motion to the fork framework. The combined effect of the cam and crank is to lower the fork framework into the bowl and move it forward a distance of about 8 in. towards the press rollers, then raise it out of the water and move it quickly back to the starting point. Owing to the variation in the leverage of the crank when acting upon the slotted lever, the forward stroke is very slow, while the backward stroke when the forks are above the water is very quick.

The bottom squeeze roller, which is usually of solid steel covered with brass, is positively driven by means of gear wheels. A belt from the line shaft drives the pulley, which gives motion to the gear wheel fixed on the end of the squeeze roller. The top roller, which is covered with roller lapping to obtain a resilient surface, is, when covered, nearly the same diameter as the bottom roller. It is normally driven by frictional contact with the lower one, being pressed

down and kept in contact with the bottom roller by means of weights and compound levers acting through springs, so that a very powerful but springy grip is obtained. The arrangement is as follows: The lever, which is fulcrumed at the back, exerts pressure on one end of

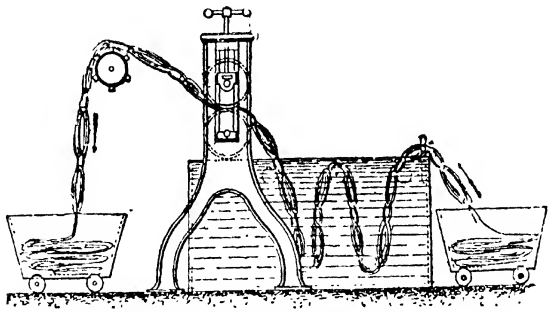

FIG. 57.—Scouring Machine for Chain Yarn.

the top squeeze roller through the rod, which carries the required number of weights and exerts a downward pressure on the lever. The latter has connected to it near its fulcrum a connection rod, which by means of a spring at the top transmits to the top roller the total pressure exerted.

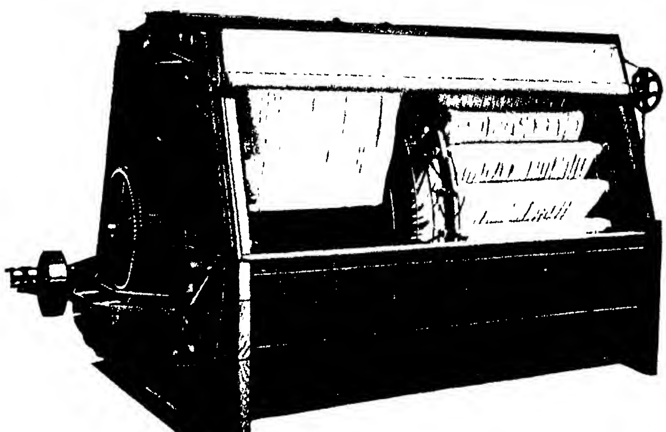

FIG. 58.—Revolving Type Yarn Scourer (Klauder-Weldon).

There is a tendency when a fairly large lump of wool arrives at the nip of the squeeze rollers for the top roller to be stopped, since it is normally driven by friction, and for the wool to be ground between the stationary and the revolving roller. A special motion termed

a catch-box or escapement motion is introduced, by means of which the top roller is positively driven from the bottom roller, when the former ceases to revolve, by frictional contact alone. The motion consists of a clutch which is placed on the projecting shaft of the top roller, the outside half of which is loose on the shaft, and has compounded with it a gear-wheel which is driven by a gear-wheel on the shaft of the bottom roller. The number of teeth in the driven wheel being 20, and the number of teeth in the driver 18, thus the top roller when rotated from the bottom is rotated at a slower speed. Further, the bottom roller also has a slightly larger diameter than the top one; therefore the latter has a correspondingly greater speed when driven by friction. The inner half of the clutch is keyed

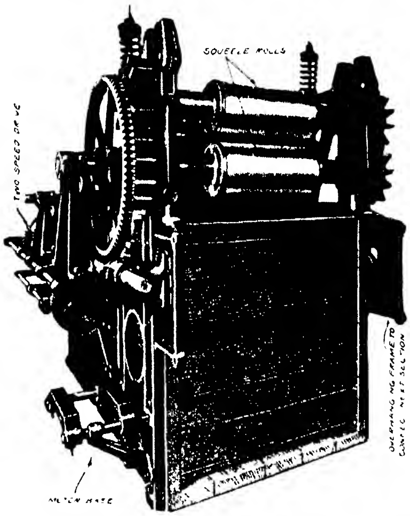

FIG. 59.- Apron Type Yarn Scourer (Klauder-Weldon).

firmly to the shaft of the roller, and the teeth of the clutch are so arranged that when the roller is working normally the fixed half of the clutch is being driven at a greater speed than the loose half, and gains tooth by tooth on the driven and loose half. As it is mounting the points of the teeth on the loose half the latter is pushed against the power of a strong spring a sufficient distance along the shaft. When a lump of wool stops the rotation of the top roller, the loose half gears with and drives the fast half, and hence drives the top roller until the lump has passed through and the roller is being again driven by friction.

An arrangement is also provided for easing the pressure on the top roller when the machine is standing. It consists of a short shaft which extends across the width of the machine and which carries a handle at one end. Two worms are cut on this shaft, which engage

with two worm wheels that are suitably fixed to short shafts, one of which, for one side of the machine, is shown. A similar arrangement is fixed on the other side of the machine, since the weighting arrangement is duplicated for the other end of the squeeze rollers. To each of these shafts is attached a chain, one end of which is connected to the levers, so that by turning the handle in the proper direction the chains are wound on their respective shafts and the pressure removed from the roller ends.

Another form of rake machine is the so-called chain harrow scourer.[3] The fork action in this is quite different, for while in all other types the forks or harrows propel the wool forward, in the chain

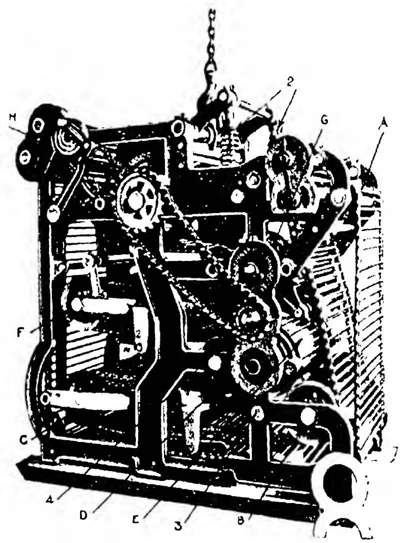

FIG. 60.—Apron Scourer Showing Inside Mechanism.

system the forks hold or retard the wool, the propelling agent being the flow of sud from the pipes and pump, so arranged that the flow of sud travels at a quicker rate than the surface speed of the harrow, assisted by the slightly slanting position of the top bowl. This allows the scour or sud to pass into contact with every portion of the wool whilst it is retarded by the forks of the harrow.

According to the theory of wool scouring, this should greatly reduce the tendency to felt, as the wool is gently floated towards the delivery rollers, and does not come into contact with any disturbing influence. Thus the staple formation of the wool and straightness will not be disarranged to a large extent. This is a good feature, as the less the staple is disturbed, the less time, expense, and machinery are required to rearrange the fibers in the succeeding operations.

[3] *Text. Mfr.*, 1921, p. 67.

As the greasy wool leaves the feed lattice, figure 51, it comes under the action of the shower of sud from the pump. The pipe passes the sud from the lower bowl and allows it to be discharged on to the wool in a manner to carry the wool forward. To check the too rapid motion of the wool the chain harrow forks intervene, and by traveling at a slower speed than the flow of the sud they retard the wool and allow the sud to pass through it. The chain harrow comprises the sprocket wheels which support and control the chain to which are attached the prongs. To prevent the sud overflowing the top tanks, overflow pipes are provided, and are regulated by the handwheel, which is set according to the quantity of sud passing into the top tank. During the passage of the wool from the feed to the delivery end of the tank, any heavy impurities which fall pass direct to small settling tanks which are separated from the scouring portion by means of perforated brass plates. As the wool reaches the press rollers it passes over the incline which prevents the dirty scour passing back to the scouring tank and allows it to go direct into the bottom tank for settling. The pressure on the rollers is controlled by weights operating through the weight rod bottom lever and the spring rod. The pressure may be regulated by means of the handle.

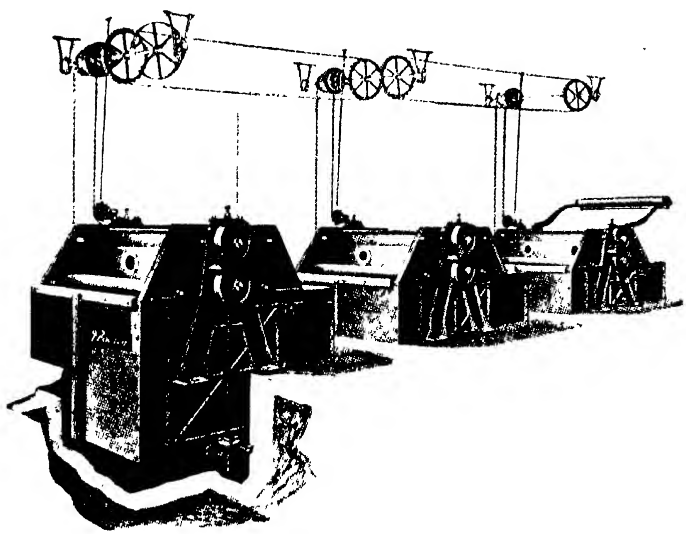

FIG. 61.—Iron Bowl Scouring Machine for Linked Skeins (Proctor & Schwartz).

Another type of wool-scouring machine has been designed for the purpose of giving a minimum amount of agitation to the wool, the liquors themselves being circulated through the machine. One

form of machine is so made that the wool is packed in large cages in pairs so arranged on a pulley that they mutually balance each other. While one cage is immersed in the scouring-bath the other cage is out of the liquor, which drains down through the wool back into the bath. This operation is kept up continuously until the wool is thoroughly scoured, when the cages move on to the washing-bath, in which they are manipulated in the same manner.

2. Machinery for Scouring Yarn.

In former years yarn scouring was conducted altogether by hand, the hanks of yarn being hung on sticks and suspended in the scouring bath, and being turned from time to time until thoroughly cleansed. A great deal of yarn scouring is still done in this manner, especially

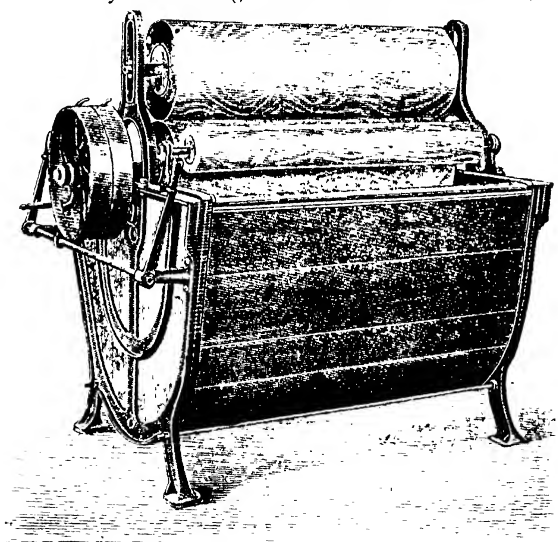

FIG. 62.—Open Width Scouring Machine for Cloth.

in small establishments and where coarse yarns are dealt with. The general tendency, however, is now to conduct the scouring of yarn by means of special machinery, as the output is greatly increased, the yarn is scoured with more uniformity, and there is less danger of felting, and consequently the stock is kept in a better condition.

One very serviceable type of machine for yarn scouring consists of three long tanks or "bowls," the first of which contains a dirty scouring bath, the second a clean scour, and the third simply warm water to serve for washing off. The hanks of yarn are given a few twists so as to prevent them from becoming tangled, and are fed into the first tank by a traveling apron. They are carried through the liquor several times forward and backward by means of endless

bands of cross-slats. They are finally passed through squeeze rolls into the second tank which they traverse several times in the same manner as before, and so on through the last or washing tank. When delivered from the last tank they should be clean and free from soapy liquor. The hanks are then hydro-extracted and are ready for dyeing, bleaching, etc.

Yarn may also be scoured very satisfactorily on such machines as the Klauder-Weldon dyeing machine. In this case the yarn is stretched on the rods of the machine and is maintained in a state of

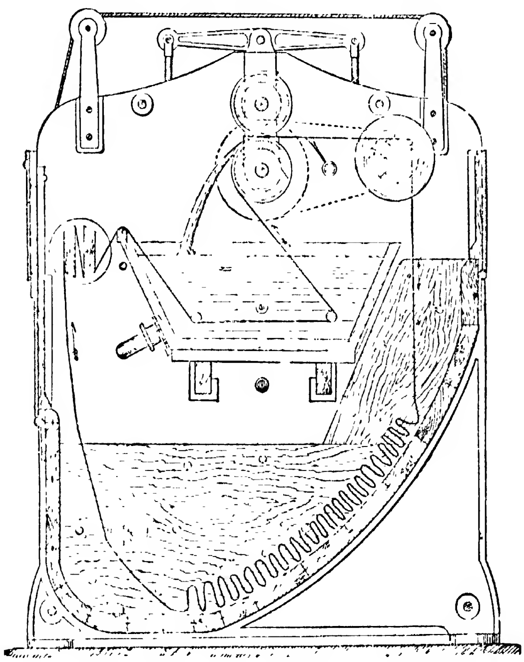

FIG. 63.—Dolly Scouring Machine for Cloth.

slight tension during the scouring, which tension may be regulated to any desired amount. In this manner any undesirable curl is removed from the yarn, and if the dyeing operation is to follow immediately after the scouring, the yarn need not be taken from the machine, but may be washed and dyed thereon through continuous processes. Such a machine is especially suitable for fine single worsted yarns which are liable to felt, as the yarn is always in the stretched condition and rotates with the machine through the bath without any opportunity to felt. The scouring bath may be pumped to a reservoir tank, and the yarn is then washed in warm water. This method affects great economy of handling and also of time.

Wool yarn may also be scoured in what is known as the chain form; that is, the hanks are loosely tied together in the form of a long continuous chain, and passed through the scouring bath, being drawn along by passing through a pair of squeeze rollers at one end of the scouring tank. The chain of hanks is passed through several times

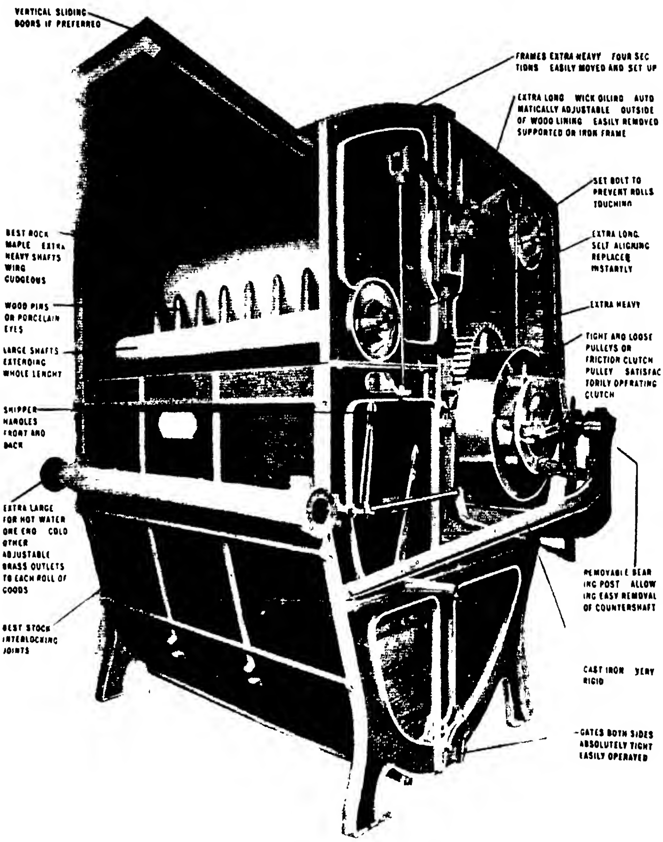

FIG. 64.—Scouring Machine for Cloth (Rodney Hunt).

until the yarn is thoroughly cleansed, after which it is washed off in the same manner by passing through warm water. This method of operation has its drawbacks; in the first place, there will always be slight unevenness of scouring at the points where the hanks are tied together, by reason of the tie-bands choking on the yarn and preventing good contact with the soap liquor; this will be true also in the

washing. Again, as there is a good deal of mechanical friction on the yarn, there will be great liability to felting, and for certain grades of yarn the process would be totally unsuitable.

3. Machinery for Scouring Cloth.

Cloth is scoured altogether by machinery. The simplest form is a wooden tank or bowl across which is placed a revolving winch; the cloth being carried through the scouring bath and around the winch until properly scoured, after which it is washed off in the same manner. This character of machine, however, is suitable only for very light weight and easily penetrated materials. For heavier goods it is necessary to have a machine provided with squeeze rolls and scrubbers in order to effect a thorough cleansing of the cloth. These cloth scouring and washing machines are usually called "dollies."

Chapter VII.

By-products in Wool Scouring.

1. By-products Obtained in Wool Scouring.

The usual method of wool scouring by means of soap solutions as generally practised is very wasteful. If reference be made to the amount and character of the impurities removed from the wool during the operation of scouring, it will at once be evident that by-products of great value could be recovered from the scouring liquors. Large quantities of soap, alkalies and fats, together with the numerous potash salts, are allowed to run to utter waste. At times the fleece is washed on the sheep's back in streams of running water; this treatment will, of course, remove nearly all of the soluble potash compounds, and also some of the fatty matters which may be emulsified by the water. Except in so far as these materials may fertilize lands watered by the stream, they are completely wasted in an economic sense. In the same manner little or no use is made of the waste scouring liquors in the vast majority of our mills. But the fact is becoming more and more apparent to the progressive manufacturer, that either the system of wool scouring must be changed over to the solvent process or that a method of working up these by-products in an economic manner must be devised.[1]

[1] The treatment of waste liquors from wool scouring is a matter which has attained considerable importance at the present time, owing to the necessity of preventing stream pollution. The waste scouring liquors are particularly offensive in this respect as they contain a large amount of sticky fatty matters together with considerable organic matter which undergoes decomposition and soon becomes very foul. The fatty matters include both the grease from the wool and the fatty acids of the soap. In America where the suint is removed at the same time as the grease, the waste liquors will also contain the potash salts of the wool, and if these were in a suitable form they would be valuable fertilizer. Unfortunately the presence of the grease does not allow of the direct use of the waste liquors for this purpose.

In the treatment of waste scouring liquors the main purpose is to remove the greasy matters, and then to so purify and filter the solution as to render it innocuous when run into rivers or streams. There are two general processes of treatment in vogue: (a) the acid process, and (b) the lime process.

In the acid process the waste liquor is mixed with the required amount of dilute sulfuric acid. This may be waste acid liquor from carbonizing or from dyeing; or a solution of nitre cake (sodium bisulfate) may be used. Sufficient acid is added to cause complete precipitation of the fatty acids of the soap. The liquor is then filter pressed and the clear filtrate run to waste The grease left as filter cake may be purified and used for making low-grade soap.

In the lime process the waste liquor is mixed with milk of lime, which causes the precipitation of the fatty matters as an insoluble lime soap. The lime process also brings down the emulsified wool grease more completely than the acid process, though this is best done in either case by the use of a suitable coagulant such as alum. The lime soap may be filtered off and treated with hydrochloric acid, if desirable, for the recovery of the fats. Or the filter press cake may be mixed with coal and used for fuel.

The cost of purification of waste scouring liquors is usually a good deal more than can be gotten back from the sale of the recovered fats. This is due to the large volume of liquors which have to be handled, settled and filtered. There is seldom more than 0.1 to 0.2 percent of fat in the waste liquor, and there are so many other impurities that the crude fat is very low grade in quality and needs considerable purification to make it commercially useful.

The following table gives the analyses of several liquors from wool scouring (in grains per gallon):

	1	2	3	4
Total solids	1380	758	1246	685
Grease	635	518	653	476
Alkalinity as sodium carbonate	132	113	214	102

2. By-products from Steeping Liquors.

In places where a steeping operation previous to the soap scouring is carried out, the potash salts from the steeping liquors may be worked up; but usually the cost of evaporating such large quantities

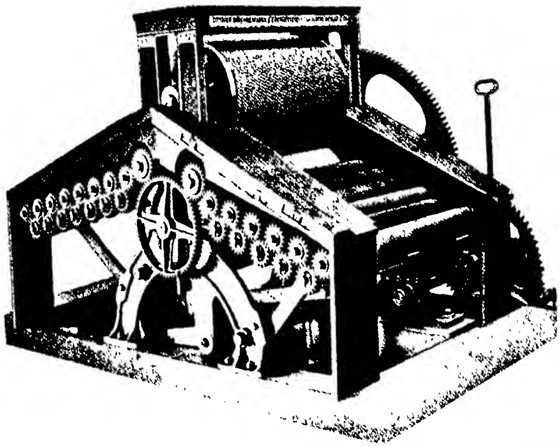

FIG. 65.—Large Size Squeezer for Skein Yarns (German Type).

of water is too great. In order to reduce the cost of subsequent evaporation to a minimum, the steeping with hot water should be cumulative; that is, the water should be pumped through a series of tanks in such a manner that the dirtiest water meets the dirtiest wool, and the wool as it leaves should last come in contact with fresh clean water. By causing the water to circulate through the material again and again and to extract fresh quantities of wool, a rather saturated solution of suint can be obtained. This solution containing a large proportion of potash salts, together with a certain amount of emulsified grease, forms an excellent fertilizer, and can be used directly for this purpose if so convenient. If, however, it is desired to recover the potash salts themselves, the saturated steeping liquors are evaporated to dryness. This is done most economically by utilizing the waste heat from the furnaces and boilers. Should potassium carbonate itself be desired, it will be further necessary to calcine the evaporated residue in suitable furnaces. As the dried suint contains a large

proportion of organic matter, a considerable quantity of gas will be formed if the calcination is conducted in retorts. This gas may be utilized for illuminating or for fuel purposes. The calcined residue will consist for the most part of potassium carbonate, together with small amounts of the chloride and the sulfate of potash. This system has been practised successfully in Belgium and it has been found that 1,000 pounds of raw wool will yield about 100 pounds (or 10

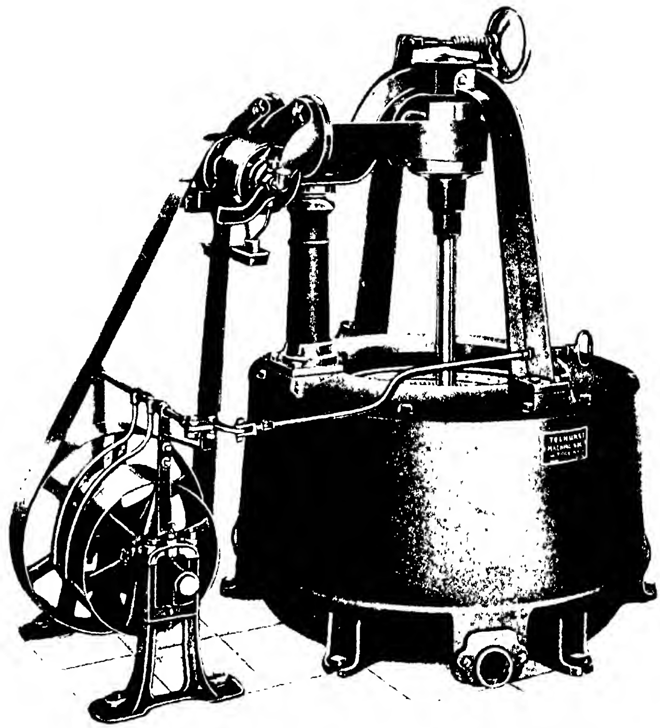

FIG. 66.—Centrifugal Extractor, Overhead Belt Driven (Tolhurst).

percent) of potash salts; 80 to 90 pounds of this being the carbonate. The yield, however, will depend very largely on the nature of the wool and the method of washing; and the average yield will not, perhaps, be more than five percent on the weight of the raw wool. The potash thus obtained is, of course, in a very crude condition, being mixed with dirt, etc., present in the wool. It may be purified by lixiviation with water and subsequent evaporation, such as practised in the alkali industry. It is doubtful, however, if the purification of this salt could be effected in a paying manner. The crude product obtained by evaporation of the steeping waters also contains a con-

siderable amount of nitrogenous matters, and it may be utilized for the preparation of potassium ferrocyanide by fusing with scrap iron, and extracting the resulting mass with water, and finally obtaining the ferrocyanide or yellow prussiate of potash by crystallization.[2]

There have been several forms of steeping tanks devised for the purpose of saving the steeping waters from wool in order to recover the potash salts. The following arrangement has been designed by Fisher, and is in use to some extent on the continent of Europe where the steeping process is carried on. In figure 74 are represented four large iron tanks of a cylindrical shape, suspended between two large

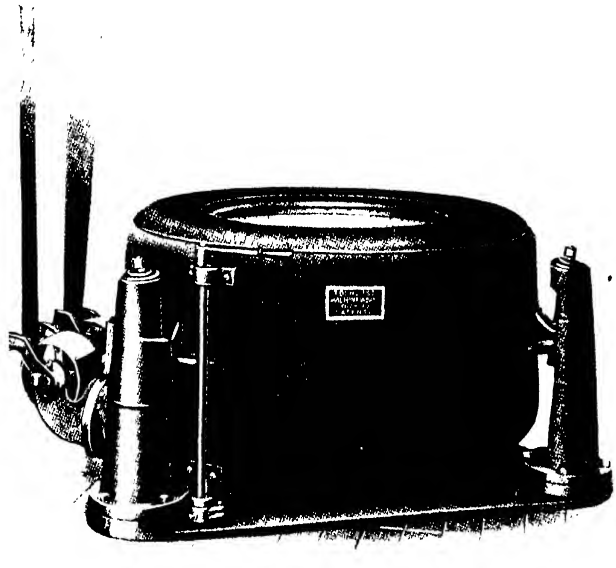

FIG. 67.—Centrifugal with Under Drive (Tolhurst).

wheels and capable of being revolved around a common axis at E. Each tank can thus be raised to a higher level for the purpose of draining the wool it contains and running the liquor into the next tank. The tanks are each filled with wool, and the first one is then filled up with tepid water and the wool allowed to steep for several hours. The liquor is then run into the second tank where it is kept warm and allowed to remain for several hours again. In like manner the liquor is run to the third and fourth tanks until it finally becomes saturated with extracted matter, when it is ready for evaporation and calcination in order to be converted in potassium carbonate. When the liquor is

[2] It is said that certain French combing establishments produce annually about two and one-quarter millions of pounds of potash obtained from wool scouring liquors, and this is sold at prices ranging from $6.75 to $9.25 per 220 pounds.

run from the first tank, it is again filled up with fresh tepid water, and this charge also passes through the series in the same manner as before. These operations are repeated until all of the soluble matters are dissolved from the wool. The tanks are then emptied and filled with fresh lots of raw wool. In the proper working of the process after it has once been put in operation, the greasy wool is first

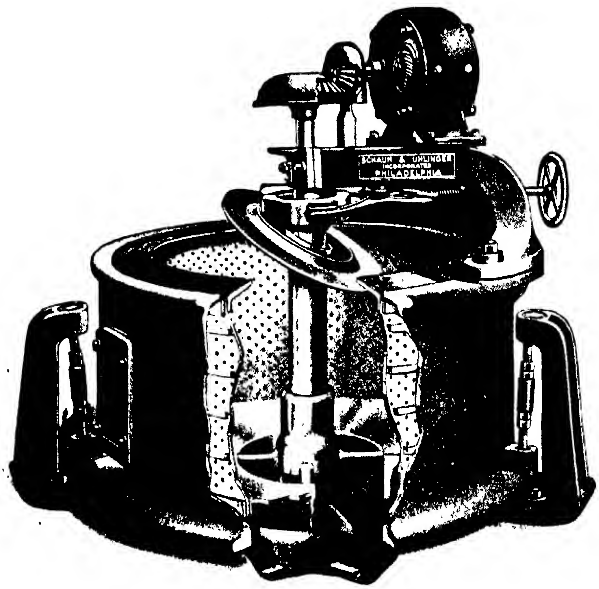

FIG. 68.—Centrifugal Extractor with Electric Drive (Schaum & Uhlinger).

washed with water already fairly well saturated with extracted salts, and then next with weaker solutions, until at last the nearly extracted wool is washed with pure water. To an American this process of extraction would hardly appeal as being at all practical, as the time required for the process would be far too long, but where work can be run along continuously and labor is not especially dear, such a process might be made profitable.[3] Havrez gives the following

[3] According to Chandelon, 1,000 kilos. of raw wool will furnish about 313 liters of steeping solution of 1.25 sp. gr., having a value of about $3.75, whereas the cost of extraction will not exceed 60 cents. From a report of the Dalry Works, in Ayrshire, where the waste scouring liquors are worked, it appears that from the suds produced in the scouring of wool, 6,000 to 7,000 gallons produced about 700 pounds of grease, valued at about $30.00 per ton. The same amount of suds yield weekly about 1,000 pounds of potash, valued at about $82.00 per ton, and about 200 pounds per week of the combined sulfate and chloride of potassium, valued at about $35.00 per ton.

table showing the amount of dry matter in steeping solutions at different degrees of concentration:

Sp. Gr. of solution	Degrees Tw.	Salts per liter, Gms.
1.377	75.4	769
1.215	43.0	376
1.102	20.4	175
1.048	9.6	72
1.025	5.0	37
1.012	2.4	17
1.006	1.2	8

FIG. 69.—Hercules Type Centrifugal Extractor (Gillespie).

The method employed at these works for the recovery of th grease and potash from the wash waters is as follows: The suds fro the first scouring bowl, containing about nine-tenths of the grease an potash, after standing about twelve hours to insure deposition of th

sand and dirt, are evaporated in a pan until the liquid attains a syrupy consistency. The resultant liquid is then cooled in shallow iron trays, and the grease which collects on top is removed at intervals. The semi-liquid residue is then calcined in a brick oven, and the heat produced from its combustion is utilized to assist in the evaporation. A crude potassium carbonate is thus produced, which after complete carbonation is boiled with water to dissolve out the potash salts. The solution is then concentrated to 100° Tw., when the potassium sulfate and chloride crystallize out on cooling.[4]

In a type of machine in use at the works of Emile Richard-Lagerie, of Roubaix, France, the wool is treated successively to the action of liquors of diminishing strength, the last being clear water. After passing through the wool the liquors are pumped into tanks for redistribution until they reach a density of 1.07, when they are evaporated and the residue calcined for the manufacture of potassium carbonate.

3. By-products Obtained from Scouring Liquors.

In the waste scouring liquors the chief materials present are fatty matters and soap. These liquors have, perhaps, received more attention as materials for the recovery of by-products than the steeping liquors, chiefly for the reason that in most localities the steeping operation is omitted, and secondly, because of the pollution to streams caused by the influx of such scouring liquors.[5]

The following table, which is taken from the results of actual experience, shows the analysis of several samples of scouring liquors from raw wool:

	1.	2.	3.	4.
Water	99.38	97.10	96.50	97.80
Mineral matter	0.15	1.05	1.30	0.60
Oil or grease	0.27	1.20	1.52	1.36
Other organic matter	0.20	0.65	0.68	0.24
Pounds of sulfuric acid required to neutralize 1000 gals.	7	14	44	22
Pounds of recovered fat per 1000 gals	27	120	152	136

There are several methods in use for the treatment of such scouring liquors, chiefly with a view to the recovery of the soap and wool-fat. It must be borne in mind that these liquors contain all of the soap originally employed in scouring, the fatty matters from the wool in

[4] Havrez has calculated that the money value of steeping liquors when employed for the manufacture of potassium ferrocyanide is more than twice that of their ordinary commercial value. His experiments have shown that with the potassium carbonate obtained from 100 kilos of the ignited residue of wool yolk there is associated about 17.3 kilos. of potassium cyanide, which is capable of yielding 19 kilos. of potassium ferrocyanide valued at about $6.50.

[5] Various methods have been suggested for the treatment of soap liquors from wool scouring for the extraction of the fatty matters, and in many cases the processes given are perhaps more interesting as curiosities than as successful commercial methods. According to Baudot (*Fr. Pat.* 413,442) the soap liquors are separated from the wool and collected in special tanks where they are vigorously beaten in order to emulsify the fatty matters. The same pump which beats the liquor also delivers it to a separating tank from which the fatty matters, which then float on the surface of the liquid, are removed, while the liquor passes into an electrolysing apparatus where it is regenerated for further use (*sic*).

the form of an emulsion, the potash salts of the suint, and the heterogeneous dirt which is always present in the fleece.[6]

A process which finds favor to some extent in certain establishments is to precipitate the soap and fatty matters by either the addition of milk of lime or calcium chloride. The magma of lime soap

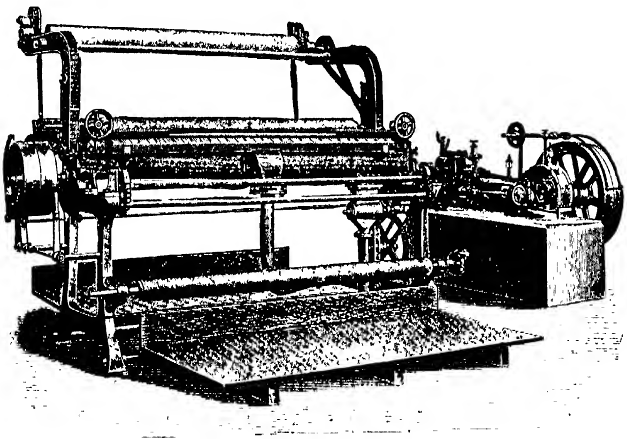

FIG. 70.—Open Width Vacuum Extractor for Cloth (German Type).

and grease so obtained may be decomposed by hydrochloric acid, and the liberated fatty acids and grease collected, purified, and utilized for the manufacture of soaps under the name of "recovered grease." Or the lime magma may be directly mixed with coal and calcined for the purpose of producing illuminating gas. It is said that about one-third of the cost of the soap used in scouring may be recovered in the value of the gas so produced.

[6] The waste liquor from washing most wools is rich in fat abstracted from the wool and soap. It is not sufficiently profitable in many cases to make it worth while treating the waste liquor; but it is forbidden by many corporations to turn untreated waste liquor into streams, rivers, or sewers. In the oldest and still the largest-used method, which is known as the Magma process, the waste liquor from the scouring machines is run into a sufficiently large tank, and sulfuric acid is added until all the alkali which is present is neutralized The whole is then well stirred, so that all the acid is utilized, since if the acid is added and no stirring is done, it simply sinks to the bottom and very little is utilized. It is a good plan to add the acid in very small quantities at the time the liquor is being run into the tank, so that as nearly as possible all the grease will be separated, and no acid will be left in a free state. If acid is present in a free state it renders the effluent acid, and tends to carbonize the grease, in addition to its being wasted. The liquor is now left to settle, and the liberated grease rises to the top, the heavy dirt falling to the bottom, leaving the acid water in the center. The acid water is piped out and run through a layer of lime into the sewer, while the grease is pumped out into another tank which acts as a drainer or filter, the bottom of which is laid with sawdust, ashes, or any other cheap filtering medium. The remaining water drains away and the grease solidifies, and is then cut into blocks which are wrapped in coarse packing cloth. These are then placed in layers between plates inside a steam-heated ovenpress which is worked by hydraulic power. As a result of pressing, a stream of dark-brown oil and water runs out of a pipe at the bottom of the press into a tank, where the oil and water separate themselves. The oil is pumped from this tank into a purifying tank, where the grosser impurities are taken out. The oil in its most impure form is termed black oil, and when slightly purified it is termed brown oil. Both kinds of oil are used in the shoddy and mungo trade for oiling these materials. The residue after the pressing is used largely for manure.

Lewkowitsch has made the following observations on *recovered grease* or *Yorkshire grease,* obtained from the soap suds used in wool scouring. He classified the constituents of the recovered fat under three heads: (*a*) Free fatty acids resulting from the decomposition of the waste soap, with mineral acid, and partly owing to the existence as a free fatty acid of the wool-fat. (*b*) Neutral (that is, saponifiable), fats; consisting of the real saponifiable constituents of the wool-fat, and the esters, etc., of the fatty acids of the fat. (*c*) Unsaponifiable matter which may consist of the free alcohols which are character-

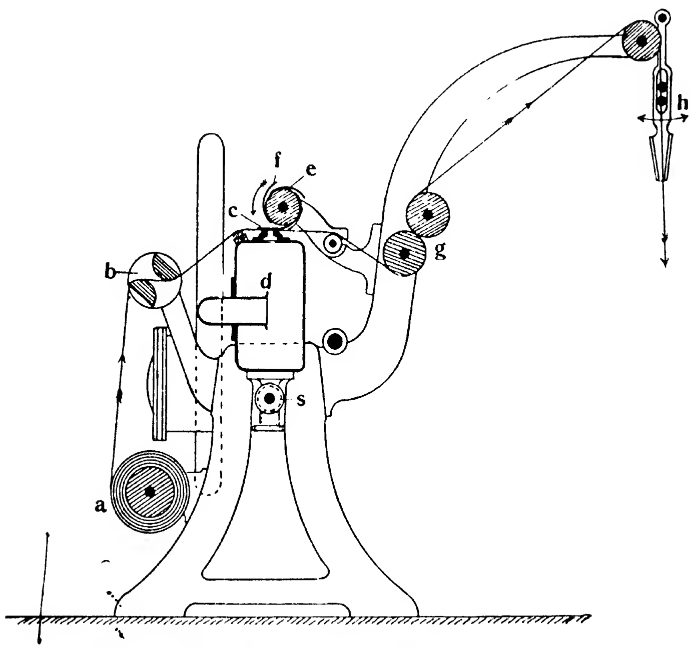

Fig. 71.—Cross-section of Open Width Vacuum Extractor.

istic of wool-fat, together with hydrocarbons which were present in the oil employed for greasing the wool. The molecular weight of the free fatty acids was determined by titration with semi-normal caustic soda solution, and was found to be 345. This was rather a high figure, but further investigation showed the fatty acids to consist of two series, the one giving a molecular weight of 326 and the other of 520. These fatty acids formed two different soaps, which resulted in the precipitated fatty acids consisting of 9 parts of the first series and 1 part of the second series. The neutral fats of the recovered grease, which are the chief constituents of wool-fat, contain cholesterol and isocholesterol alcohols, as well as other unidentified alcohols. The complete analysis of the recovered grease was as follows:—

	Percent
Volatile acids	1.28
Insoluble free fatty acids	20.22
Combined fatty acids	48.47
Combined alcohols	31.32
Unsaponifiable matter	5.15

According to Hurst,[7] the following method used in many mills in Yorkshire for the recovery of grease from the waste scouring liquors: The soap suds are collected in a large tank calculated to hold a day's supply (from 6000 to 8000 gallons of liquor); though usually two tanks constructed of brickwork or concrete are provided, one tank being used to collect the suds while the treatment of the suds of the preceding day is carried out in the second tank. Brown oil of vitriol, or, preferably, hydrochloric acid, is added to the suds, and after thorough agitation of the mixture it is allowed to settle; the fatty matters rise to the top and are skimmed off, and thrown on to large cloth filters to drain. The fat thus collected is known as "magma" or "sake,"[8] and is sent to the grease mills while the residual liquor is run into the river. The magma is then put into bags and piled up in a tank and weighted, and so left over night, when a large quantity of water is pressed out; the cakes of magma are then put into a filter press kept hot by steam, when a dark greasy product is pressed out, and comprises the Yorkshire grease. The solid matter left in the press is known as "sud-cake" and is employed as fertilizer, for which purpose it has considerable value.

Yorkshire grease is usually of a brown color, though sometimes almost black; it is of a sticky consistency and has a melting point of about 44° C. It easily undergoes saponification with soda or potash, but the soap so formed is not very soluble in water and is very short-grained. From the analysis given above it will be noticed that Yorkshire grease contains a considerable amount of free fatty acids and also a high percentage of unsaponifiable matter, the latter containing cholesterol, and being derived from the natural grease of the wool and also from the mineral oil which may have been used in the oiling of the wool stock. The character of the free fatty acid will vary with the kind of soap employed in scouring.[9]

Yorkshire grease is generally purified by distillation by heating with superheated steam. The principal product which distils over is a thin limpid oil of a pale yellow color, which on cooling solidifies into a pale yellow grease, known as "first distilled grease"; this requires from 20 to 24 hours to distil over. The next fraction consists of

[7] For an excellent article relating to the preparation of Yorkshire grease and the products obtained from it, see Hurst, *Jour. Soc. Chem. Ind.*, 1889, p. 90. The author is indebted to this article for much of the matter in the following résumé.

[8] The operation of treating the suds with acids is commonly known as "saking," probably being a local corruption for "seeking."

[9] As the crude grease is sometimes employed in the manufacture of lubricating greases, the following factors in this connection are given:

	°C.
Vaporising temperature	182
Flashing point	220
Fire test	248

a greenish oil and is collected separately and called "green oil" or "crude grease" and is usually sent back to the stills with fresh quantities of grease, or made into light lubricating oils. The residue left in the stills is known as pitch.[10] The first distilled grease may be sub-

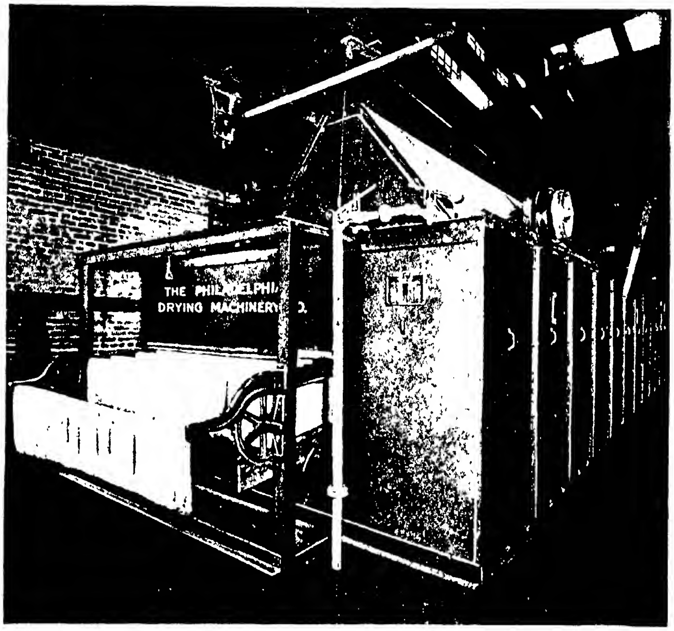

FIG. 72.—Automatic Yarn Dryer with Thermostatic Control (Phila. Drying Mchy. Co.).

jected to a second distillation, whereby there is obtained a "second distilled grease" and a small residue of pitch. The distilled greases[11] are cooled slowly in order to cause the stearin they contain to separate in a granular form while the olein remains liquid. These two are then

[10] The following table shows the products obtained by the first distillation of Yorkshire grease:

	Percent
Water and loss	20.76
Spirit oil	4.10
First distilled grease	45.54
Green oil	15.47
Pitch	14 13

Some kinds of grease do not give any of the spirit oil fraction, while others yield but a small amount. This spirit oil is of a pale yellow color, becoming in time reddish brown, it has an unpleasant empyreumatic odor, and is readily inflammable

[11] The distilled greases are of a pale yellow color and are granular in structure. Hurst gives the analyses of two samples of these substances:

	First Distilled Percent	Second Distilled Percent
Water	0 98	1.04
Free acid	62.12	66.56
Unsaponifiable matter	12 88	13 24
Neutral oil, etc.	23.02	19.16

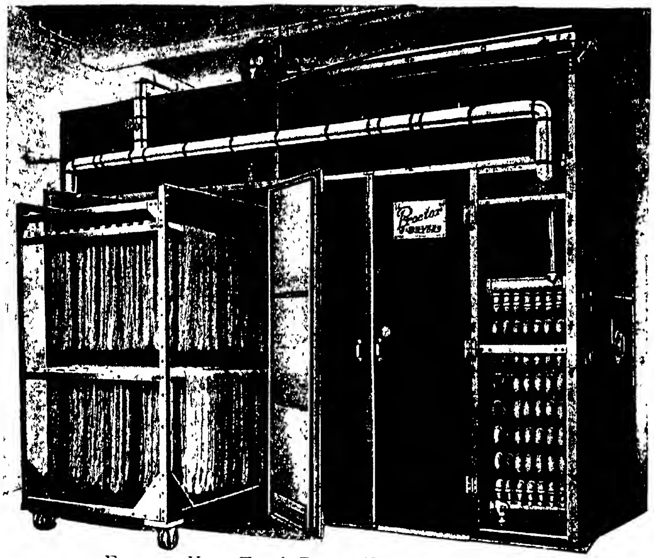

Fig. 73.—Yarn Truck Dryer (Proctor & Schwartz).

separated by pressing in canvas cloths, whereby about 6 percent of olein[12] and 44 percent of stearin[13] are obtained.

An analysis of the oil obtained from the distillation of the recovered grease gave the following:—

	Percent
Free fatty acids	54.91
Combined fatty acids	7.02
Combined alcohols	4.26
Hydrocarbons	34.54

[12] The olein so obtained is better known as "wool oil" and comes from the press as a pale colored body which gradually assumes a brownish color, probably due to the presence of iron. This product is chiefly employed for the oiling of wool stock, but is also used to some extent for the making of soaps and for lubricating greases. Its composition varies considerably; the following analyses of typical samples are given by Hurst:

	1 Percent	2 Percent	3. Percent	4. Percent	5. Percent
Water	1.12	2.33	1.38	2.51	....
Free acid	56.06	56.26	53.05	59.83	64.42
Unsaponifiable oil	34.66	29.46	16.32	38.92	9.95
Neutral oils	9.20	11.95	28.65	....	25.63

[13] This stearin is a hard pale yellow greasy solid; the product from the first distillation has a darker color, has a higher melting point and contains less fatty acids and more oil. Hurst gives the following analyses of this material:

	First Distilled Percent	Second Distilled Percent
Water	0.6	1.48
Free acid	88.6	76.3
Unsaponifiable oil	0.49	0.4
Neutral oil	2.11	7.7
Solidifying point	45°C.	53.5°C.
Melting point	48°C.	57°C.

This stearin when saponified with soda gives a soap forming an exceedingly gelatinous mass with water, and from which it is very difficult to extract with ether any mineral oil which may be present; thus, it is possible to mix with this stearin 25 percent of paraffin oil, and yet on saponification, no separation of mineral oil occurs. On this account, wool grease stearin is of much value in the preparation of sizing tallows; on the other hand it is a poor material for making soaps.

Of the large percentage of neutral fat originally present in the recovered grease, scarcely any remains after distillation, it being broken up into fatty acids, while the esters absorb oxygen during the distillation and are converted into hydrocarbons.

Another process is to treat the scouring liquors with sulfuric acid, which causes the fatty acids to separate, and together with the wool-fat, to rise to the surface in the form of a scum or magma. This is filtered, and the crude grease so obtained may be used for the manufacture of soap; but the product is of such inferior quality that this procedure is not recommended, and a further purification of the grease is desirable. The magma may be pressed between hot plates, and the liquid wool-grease extracted in this manner. This comes into trade under the name of "Yorkshire Grease," and may be used as a lubricating oil, or for smearing sheep in cold weather. The magma may also be distilled in a current of steam, whereby stearin and olein are obtained in a pure condition very suitable for the purpose of making good qualities of soap.[14]

As wool-grease is becoming of considerable importance as a by-product in the wool-scouring industry, the following note concerning its analysis will be of interest: Ulzer and Seidel[15] recommend the following process of the analysis of wool-grease: 20 gms. of potassium hydrate are dissolved in 20 cc. of water contained in a hemispherical dish of about 350 cc. capacity. The solution is heated to boiling, and 20 gms. of melted wool-grease are introduced with vigorous stirring. After boiling for a minute the dish is placed on a water bath until saponification seems complete; to make sure, however, the dish is placed for two hours inside the water oven. The soap is then dissolved in 250 c.c. of boiling water, restoring from time to time the water lost by evaporation, and when completely dissolved 40 c.c. of hydrochloric acid, slightly dilute, are added. When the fatty mass is perfectly melted, it is allowed to cool, then removed, and repeatedly boiled with water until the washings no longer show an acid reaction. After cooling, the fatty cake is removed, dried between blotting paper and finally dried in the water oven. The total acidity number is then taken by means of Benedikt and Mangold's process. Three samples of Australian wool-grease gave respectively the figures 100.2, 102.9, and 101.9. Three South American samples gave 96.4, 96.7 and 96.9. To form an opinion of the genuineness of wool-grease, it is recommended taking the actual acidity number and the Reichert-Beissl number. Its iodine absorption may also be determined.

[14] At the works of Scaife & Co., Laisterdyke, England, the following process is employed: The suds, after being run off from the washing bowl, are allowed to stand for about half an hour in a settling tank to allow of the deposit of sand and dirt. The liquor is then pumped into a tank, at the bottom of which is a system of pipes through which compressed air is forced. About 1 gallon of sulfuric acid is added to each 700 gallons of suds, and then the liquor is "blown." The violent aeration quickly brings the grease to the surface in the form of a thick foam, and a set of boards, working on an endless chain carries this froth off at one end of the tank. The foam contains only about 5 percent of water, and after collection, is treated in the usual manner for the purification of the grease.

At the works of Mattie & Co., Roubaix, France, the suds are beaten into a froth by means of a rotary agitator, which carries the fatty matters to the surface. These are skimmed off into conduits by a mechanical scraper, and are forced by a steam injector into a wooden tank, where they are heated to 140° F., and treated with sulfuric acid in the proportion of 1 pound to 100 gallons. The acid is then removed by washing, and the grease is filter pressed.

[15] *Zeit. angew. Chem.*, 1896, p. 349.

The following analysis by Hurst, shows the composition of samples of good Yorkshire grease:—

	1. Percent	2. Percent	3. Percent	4. Percent
Water	0.98	1.53	1.21	0.94
Fatty acid	18.61	24.25	24.15	26.43
Saponifiable oil	68.62	58.25	30.02	16.86
Unsaponifiable oil	11.68	15.83	44.44	55.77
Mineral matter	0.11	0.14	0.18	trace.

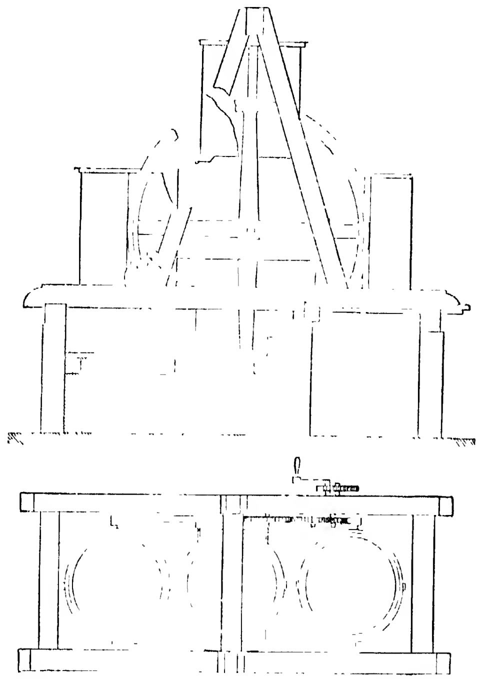

FIG. 74.—Fisher Wool Steeping Tank, Showing Elevation and Plan.

Wool-grease may also be separated from waste scouring liquors by means of centrifugation. It is by this means that lanolin is prepared on a large scale. Usually for purposes of purification, the material first obtained is emulsified with water and centrifugated again. In this manner quite a pure grease is obtained.[16]

[16] A substance known as *lanoresin*, said to be a dark colored resin, has been obtained from the waste scouring liquors from wool. It is produced in the following manner: The precipitate formed on the addition of a mineral acid to the waste scouring liquors is squeezed and mixed with 3 to 5 times its volume of benzine, heated and thoroughly agitated. During the shaking, 95 percent alcohol is added to the amount of one-tenth of the benzine; after standing for some time the liquid separates into two layers, the lower one containing the lanoresin. This is drawn off and treated in a similar manner to remove traces of grease, and finally the solvent is evaporated off. This product is designated as a gum resin, and is said to be insoluble in benzine, ether, chloroform, carbon disulfide, acetone or strong alcohol, but is soluble in water and dilute alcohol. (Feuerlin, *Eng. Pat.* 18,642 of 1889.)

Chapter VIII.

Bleaching of Wool.

1. General Remarks on Wool Bleaching.

Wool is usually bleached by the use of sulfurous acid. This compound may be used in a variety of forms; (a) in the gaseous state as sulfur dioxide, SO_2; (b) as a solution of sulfur dioxide in water, and (c) as a solution of sodium bisulfite, $NaHSO_3$. The former process is the older method, and is still the one mostly in use.

This method of bleaching wool is essentially a proces of ***reduction;*** for whichever one of the three methods above given is employed, the reduction consists ultimately of the reduction of the coloring matter by means of sulfurous acid, SO_2, as follows:

$$H_2O.SO_2 + O = SO_3.H_2O \text{ or } H_2SO_4$$

That is, the sulfurous acid is converted into sulfuric acid by combining with oxygen at the expense of the coloring matter. If the gaseous sulfur dioxide, SO_2, is employed, it is used in the presence of moisture, hence we have really sulfurous acid, H_2SO_3. As sodium bisulfite in solution may be considered as a mixture of sodium sulfite and sulfurous acid:

$$2NaHSO_3 = Na_2SO_3 + H_2SO_3,$$

we have practically the same condition to consider; and even the sodium sulfite becomes reactive in the same manner when treated with an acid, as is the case in this method of bleaching:

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2SO_3.$$

So that it may be seen that in all phases of the so-called "sulfur" bleach the active bleaching agent is sulfurous acid, the chemical reaction is a reduction process, and the final product of the reaction is sulfuric acid on the one hand and the decolorized organic body or "leuco" compound derived from the coloring matter operated upon, on the other hand.

Even under the best conditions of bleaching by the reduction process, it does not seem to be possible to obtain absolutely white wool; the fiber always appears to retain a slight yellow cast which can only be completely neutralized by means of tinting with a minute quantity of a violet coloring matter. This inability to obtain a perfectly white bleach is probably due to the fact that the compounds produced by the decomposition of pigment matter are in themselves not without a color.

It is not likely that such products resulting from the decomposition of the pigment are removed to any degree from the fiber.[1]

2. The Gas Method of Bleaching.

Bleaching by means of sulfur dioxide gas must be conducted in specially constructed chambers, usually built of stone, brick, or wood, and provided with suitable conduits for the entrance and exit of the gas. The gas itself may be obtained either by burning sulfur or by the ignition of iron pyrites. The latter compound is a naturally occurring sulfide of iron which on being burnt in suitable furnaces gives off sulfur dioxide and leaves as a residue oxide of iron.[2] At the present time sulfur dioxide gas is also to be obtained commercially condensed to a liquid form in strong steel cylinders, and this is a very convenient method of handling the article. In some forms of bleaching chambers, the sulfur is burnt directly in the room, a sufficient current of air being introduced to carry on the combustion. Usually the sulfur is contained in one corner of the room in a stone or earthenware receptacle or stove, and from this fact the operation of bleaching wool with sulfur dioxide has received the common name of *stoving*. When iron pyrites is used as the source of the sulfur dioxide, the mineral, in the form of small lumps, must be burnt in a specially constructed furnace outside of the bleaching chamber, and the fumes are led first through a dust box, and then into the chamber containing the wool. Where condensed sulfur dioxide in cylinders is used, of course, there is no need of a stove or furnace, and the current of the gas is introduced directly into the bleaching room from the valve of the cylinder. The presence of metals in the bleaching room should be avoided as the acid vapors formed therein will rapidly attack metallic surfaces, and the products consisting of metallic sulfate dropping on the wool will cause stains and spots.[3] The roof and walls of the room should also be constructed in such a manner that the

[1] An ingenious method for the bleaching of wool has been suggested by Hofmann (*Chem. Zeit.*, vol. 40, p. 1224). He proposes to "dye" the wool white by the deposition of a white pigment in the fiber. One method consists in steeping the wool in a bath containing soda ash, and then adding magnesium sulfate and warming; the result is to deposit a white precipitate of magnesium carbonate in the fiber. Better results, however, are said to be obtained by immersing the wool in a solution of cotton in ammoniacal copper oxide, and subsequently washing with water or a dilute acid, which causes the precipitation of cellulose upon the fiber. The material is finally treated with ether to render the film of cellulose opaque and white. Hofmann does not describe the purpose for which his bleached wool is to be used; it certainly could not be employed for any general textile purposes after having passed through such a ludicrous treatment as related This process has been selected as a sample of the many absurd and totally impracticable ones which are constantly being proposed by so-called chemists who seem to be totally ignorant of conditions to be met with in practice. In the field of textile chemistry, these absurd ideas are especially rampant, and many chemists (who may be very well in their own theoretical lines) seem to take it upon themselves to propose all manner of illogical innovations in a subject concerning the technique of which they are absolutely ignorant.

[2] In the burning of iron pyrites the following chemical reaction takes place:

$$\underset{\text{iron pyrites}}{2\,FeS_2} + \underset{\text{oxygen}}{11\,O} = \underset{\text{iron oxide}}{Fe_2O_3} + \underset{\text{sulfur dioxide}}{4\,SO_2}$$

100 lbs. of iron pyrites will generate 115 lbs. of sulfur dioxide, which is equivalent to about 657 cu. ft. of gas at normal temperature and pressure.

[3] In the burning of sulfur a great amount of heat is generated, and sometimes the unburnt sulfur becomes so hot that a portion of it volatilizes, and this condensing on the material being bleached may cause spots which are subsequently very difficult to remove. Danger from volatilized sulfur may be overcome by placing a shield (best made of wood covered with sheet lead and felt) in such a way that the fumes must strike the shield before coming in contact with the goods. This causes the volatilized sulfur to condense on the shield.

acid vapors on condensing cannot drop on the goods, otherwise serious damage may be the result as these condensations are in reality concentrated sulfuric acid.

The amount of sulfur consumed in bleaching wool is about 6 to 8 percent on the weight of the material, but this quantity must also bear a certain proportion to the size of the chamber.

The principle of bleaching with sulfurous acid depends on the strong reducing action this chemical manifests when in the presence of any substance capable of decomposition in this manner. A molecule of sulfurous acid gas abstracts an atom of oxygen from the compound in question (in this case an organic coloring matter) and forms

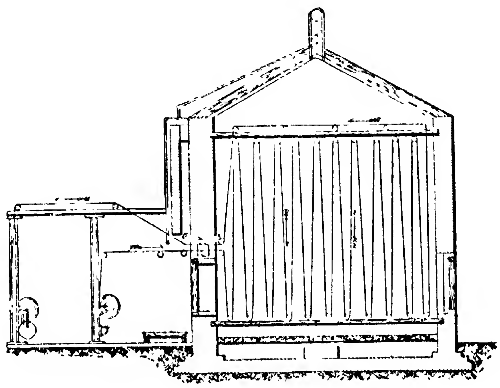

FIG 75—Sulfur Bleaching Chamber.

sulfuric anhydride, SO_3, which immediately combines with the moisture present to produce sulfuric acid; thus:

$$SO_2 + O = SO_3$$
$$SO_3 + H_2O = H_2SO_4.$$

Since the bleaching action of sulfurous acid gas in the dry state is but slight, it is, perhaps, better to assume that the reaction takes place in the following manner:

$$H_2SO_3 + O = H_2SO_4,$$

which is in reality equivalent to the simultaneous occurrence of the two preceding reactions.

In carrying this method of bleaching into practical operation, it is necessary that the wool (whether as loose stock, or in the form of yarn or cloth) should be well scoured before being placed in the bleaching chamber; and the material must be so arranged as to give the greatest surface possible for exposure to the action of the gas. It is sometimes the case, that after wool has been scoured and previous to its bleaching, it is tinted with some suitable blue or violet dyestuff in a weak soap bath. If the dyestuff so used is not decolorized by treatment

with sulfur dioxide the tint will remain after bleaching, and will give a bluish tone to the white obtained, which is more agreeable to the eye than a dead white. If the tinting is not done before the bleaching, it usually is required in goods which are to be left in the white state; not, however, for wool which is bleached simply for the purpose of dyeing it in delicate shades.

In the stoving chamber for wool bleaching considerable care must be taken to provide suitable means of ventilation so as to control the incoming and outgoing currents of air. In order to prevent drops of condensed acid forming on the roof heating coils should be suitably arranged. Furthermore, it must be borne in mind that sufficient air must be present to allow of the complete combustion of the sulfur, which otherwise might sublime in a fine powder and fall on the goods. In case the sulfur is burnt outside the bleaching chamber it is well to filter the ingoing gases through moist cloth.

When *loose stock* is to be bleached it is simply spread out on shelves arranged in the bleach-room. The wool should not be laid down too thick, and should be in a slightly moistened condition. In order to insure the equable penetration of the gas to all portions of the material, the wool should be turned over from time to time. In *yarn bleaching*, the hanks are loosely hung on sticks in the bleach-room, and no further attention is actually necessary; though in order to avoid possibility of unevenness it is well to turn the position of the hanks on the sticks. *Cloth* is bleached by hanging it in folds in open width up and down through the room over a series of rollers. In some cases, the cloth is passed through the room continuously at a slow rate of motion.[4]

In the gas process of bleaching wool the fiber acquires a harder and rougher handle and a lessened luster than is the case when bleaching with an aqueous solution of sulfurous acid. However, by treatment with a lukewarm dilute soap bath the fiber is again softened and given a pleasant handle, although this treatment tends to bring back again a yellow tinge to the wool. On this account it is, perhaps, more customary to after-treat the bleached wool with a bath of only cold water, or at best, with the slight addition of hydrogen peroxide and a trace of suitable bluing (Crystal Violet, Alkali Violet or Alkali Blue).

The time necessary to finish the bleaching will, of course, be largely dependent upon the character of the material under treatment. As a rule, about twelve hours will be sufficient under ordinary conditions; and usually the material is allowed to remain over night in contact with the gas.

It is said that gas bleaching requires from five to ten percent of sulfur on the weight of the goods; and loose wool probably requires more than yarn or cloth.

It has already been stated that sulfur dioxide is very difficult to re-

[4] In arranging woolen goods in the sulfur chamber, loose stock should be spread out on shelves, yarn should be hung on sticks, and cloth may be festooned on glass rods or enamelled sticks. When light-weight wool fabrics are to be bleached, it is possible to have a mechanical arrangement whereby the cloth is carried through the bleaching chamber continuously. It may also be remarked in the case of skein yarn and cloth, the position of the material on the sticks should be changed from time to time, or stick marks are liable to show up on the bleached goods.

move from the wool fiber; therefore, after bleaching, the goods should be very thoroughly washed.[5] But even continued washing fails to remove the sulfur dioxide as completely as is desirable, hence in some cases it is recommended to pass the material through a weak bath of chloride of lime or sodium hypochlorite. Other oxidizing agents, such as weak solutions of potassium permanganate or hydrogen peroxide, may also be used.[6] By treatment the small amount of sulfur dioxide which remains in the wool is converted into sulfuric acid, which is easily removed by washing; and then, too, its presence is far less objectionable than the sulfurous acid, as it has no bleaching action on colors. This treatment with oxidizing agents is especially to be recommended in the case of bleached woolen pieces which are to be printed in colors. Besides neutralizing the injurious effect of the sulfurous acid, treatment with solutions of chloride of lime at the same time increases the affinity of the wool for many dyestuffs. Frequently bleached yarns are woven together with those which have been dyed, and if any residue of sulfurous acid is left in the bleached wool, it will nearly always manifest its presence by decolorizing the dyed yarn with which it comes in contact. Also, on scouring, the bleached yarn will return to its natural yellow tinge. The same remarks hold of wool bleached in the loose state which is afterwards to be spun up into yarn and woven with colors, or even if it is to be subsequently dyed in the loose stock for the production of mixed yarns. Sometimes, wool is bleached after being dyed, in which case it is, of course, essential that the dyes employed should be fast to the sulfur bleach or "stoving."[7]

Of the several oxidizing agents mentioned for the purpose of removing the last traces of sulfurous acid from the fiber, the safest one by far to employ is a dilute bath of hydrogen peroxide, as in this case there is no danger of injuring the fiber by an excess of the reagent; and also excess of the chemical employed, if in turn not removed from the wool, will have no bad effect. If an excess of chloride of lime is used, there is danger that the wool fiber will be injured, and if all of the chemical is not subsequently removed by thorough washing, injurious results will follow. The same is also true of potassium permanganate, in which case, if an excess is used, the wool will turn brown from the deposition of oxide of manganese in the fiber; and then a second bath of sulfurous acid must be employed in order to remove the manganese compound. Instead of employing a solution of hydrogen peroxide directly, one may use a dilute solution of sodium peroxide

[5] The water employed for washing wool after bleaching with sulfur dioxide should be particularly free from iron. Parts of the washing or other machinery with which the goods might possibly come in contact should be protected and cased with wood. All the iron-work near a sulfur bleach plant should be lime-washed. When a sulfured piece of wool goods comes in contact with iron or with iron-bearing water a stain will usually form which is difficult and expensive to remove.

[6] Reychler (*Bull. Soc. Chim. Belg.*, 1909, p. 471) has made a detailed investigation of the action of sulfurous acid gas on wool in the presence of varying amounts of air. His results tend to show that the amount of gas fixed by the wool depends upon two factors: (a) the minor one due to "chemical absorption," and (b) the main one of absorption or solution of the gas in the fiber.

[7] The test for fastness to stoving is made as follows: a portion of the dyed wool is plaited with some white wool, moistened, and placed in a bottle containing fumes of sulfur dioxide. The bottle is corked up and allowed to stand for 12 hours, and then the sample is examined to see if the color has faded or has bled into the white.

which has been acidulated with sulfuric acid, in which case the liquid will then contain hydrogen peroxide in solution.

A convenient apparatus for use in the bleaching of wool materials with compressed sulfurous acid gas has been devised by Shaw. It is the following (see figure 76): The compressed sulfurous acid gas is contained in the cylinder A, which is connected to an expanding chamber B, and the latter in turn is connected with the cylinder C through which a perforated pipe leads up through the material to be bleached. Pressure gauges are placed on the two cylinders B and C at G. The fabric to be treated is rolled on the perforated beam P, and put in

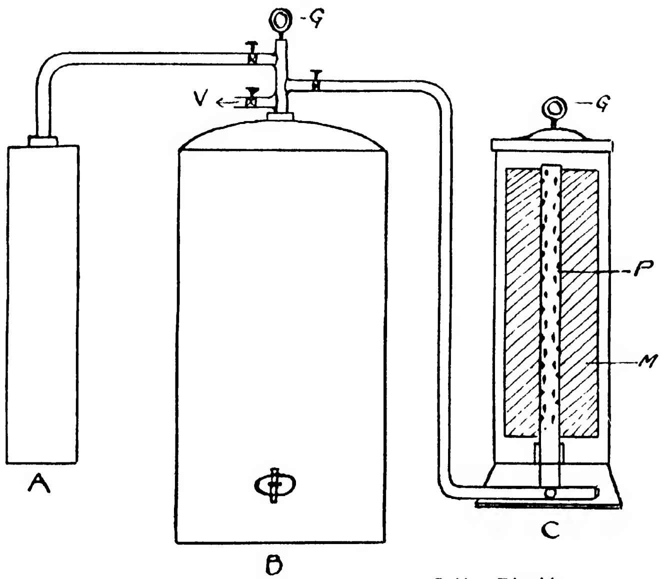

Fig. 76.—Bleaching with Compressed Sulfur Dioxide.

position in the cylinder. The connection between B and C is opened and the air is removed from the woolen material by means of the connection from V leading to a vacuum pump. When the air is exhausted, the vacuum connection is closed, and also the connection between B and C, while that between A and B is opened until the pressure gauge shows that the sulfurous acid gas has expanded into the chamber up to one atmosphere pressure. The valve between B and C is then opened, and the gas under the pressure indicated forces its way through the material to be bleached.

3. The Liquid Method of Bleaching with Sodium Bisulfite.

Instead of employing sulfur dioxide in the form of a gas, its aqueous solution may be used; or better yet, a solution of sodium bi-

sulfite in connection with sulfuric acid may be used. This method is termed *liquid bleaching*,[8] and is carried out by simply working the wool in the bleaching bath, and allowing it to steep until the process is completed, which usually requires from 6 to 24 hours, depending on the strength of the bath and the nature of the material.

The same general remarks which have been made in connection with the process of bleaching by means of gaseous sulfurous acid also hold true for the liquid method of bleaching, and the chemical principles involved are exactly the same, the only difference being in the method of applying the bleaching agent.

When employing a solution of sodium bisulfite, it is best to steep the material for 6 to 10 hours in a bath at a strength of about 2° Tw.; then squeeze, and pass through a bath of sulfuric acid at 1° Tw.[9] Sodium bisulfite in its aqueous solution may be considered in some degree as a solution of the neutral sodium sulfite together with one of sulfurous acid:

$$2\ NaHSO_3 + \text{water} = Na_2SO_3 + H_2SO_3 + \text{water}.$$

The sulfurous acid acting on the wool produces a certain amount of bleaching; and it is also probable that the sodium bisulfite itself has a certain degree of bleaching action. The bleaching, however, is not rendered complete until the wool is treated with a bath containing sulfuric acid, which reacts with the sodium bisulfite in the fiber and liberates sulfur dioxide. The efficacy of this reaction

$$NaHSO_3 + H_2SO_4 = NaHSO_4 + SO_2 + H_2O$$
$$\text{or } 2\ NaHSO_3 + H_2SO_4 = NaSO_4 + 2\ SO_2 + 2\ H_2O$$

is rendered greater by the fact that the sulfur dioxide at the moment of liberation (nascent state) is much more chemically active than in any other state; and also, as it is liberated within the innermost portions of the fibers where the solution of sodium bisulfite has penetrated. After the treatment with the acid bath, the wool should be well washed in order to remove as far as possible the excess of sulfurous acid; though, in order to remove the last traces of this chemical, as before explained, it will be necessary to treat the material with a bath of chloride of lime or other oxidizing agent.

The following practical method is given for the bleaching of 100 lbs. of loose wool by the liquid method: Prepare a bath containing

[8] It is said that the liquid process of bleaching wool does not yield the same degree of whiteness as the stoving process. In practice, however, it possesses compensating advantages, not the least of which is greater permanence, and when dry the absence of odor. The smell of sulfur, however, is generally somewhat perceptible when the goods are moist and warm. The liquid process also has the further advantages of being both economical and convenient. The greater permanency of the liquid bleach is probably due to the better penetration of the bleaching agent into the core of the fiber.

[9] The following formula for bleaching with sodium bisulfite is given:

125 galls. of water (free from iron)
10 galls. of sodium bisulfite (72° Tw.)
6 pints of sulfuric acid (168° Tw.)

The wool is placed in this bath over night, then drained well and thoroughly rinsed. Generally from 10 to 20 percent of bisulfite will be found suitable for ordinary purposes, but no positive rule in this respect can be laid down, as experience with different woolen materials alone will enable the bleacher to determine the strength and quantity of the solution to be employed in any particular case.

550 gallons of cold water free from iron, 4½ gallons of sodium bisulfite solution of 38° to 40° Tw., and 1/3 gallon of concentrated sulfuric acid. The wool is left in this bath over night, after which it is drained and then tinted in a bath containing ¾ oz. Acid Violet 6BN. It is then squeezed and dried.[10]

The process of liquid bleaching of woolen cloth is usually carried out in the ordinary cloth-washing machines, although a suitable machine specially constructed and set apart for the purpose is to be preferred. Iron parts with which the cloth may come in contact should be cased in wood, and all other iron parts should be occasionally lime-washed. Before placing in the bleaching bath, the cloth should, of course, be well scoured and washed, and then hydro-extracted, so as to remove the excess of water. If the cloth is introduced too wet it will not take up the bleaching liquor properly, and if too dry, the bleaching is liable to be uneven.

4. Use of Sodium Hydrosulfite for Bleaching Wool.

Sodium hydrosulfite is a salt of hydrosulfurous acid, prepared by the action of zinc dust on a solution of sodium bisulfite. As sulfurous acid and its salts are derivatives of the dioxide of sulfur, SO_2, so hydrosulfurous acid and its salts are derivatives of the mono-oxide of sulfur, SO. In consequence, hydrosulfurous acid would have the formula H_2SO_2, and the sodium salt would be $NaHSO_2$. Neither the mono-oxide nor the free acid has been prepared, but the sodium salt can readily be prepared in solution in the manner above described. The solution of hydrosulfite has a powerful reducing action, in which it surpasses sodium bisulfite or sulfurous acid, because while the latter will only combine with one atom or oxygen for each molecule of the reagent, the former will combine with two atoms of oxygen:

$$H_2SO_3 + O = H_2SO_4$$
$$H_2SO_2 + O_2 = H_2SO_4.$$

Sodium hydrosulfite is a salt of very unstable nature, and hence must be prepared as used, as its solutions do not keep for any length of time. Its preparation depends on the interaction of zinc with sodium bisulfite, which may be represented as follows:

$$3\ NaHSO_3 + Zn = NaHSO_2 + ZnSO_3.Na_2SO_3 + H_2O.$$

That is, three molecules of sodium bisulfite are required to form one molecule of the hydrosulfite, the remaining portion of the former salt going to form a double sulfite of sodium and zinc. A solution of sodium bisulfite is prepared so as to stand at about 60° Tw.; zinc dust in considerable excess is added, the mixture well stirred up, and then allowed to stand for a few hours in a covered vessel and in a cool place. The reaction is considered to be complete when the odor of sulfur dioxide is no longer perceptible. In order to precipitate the double zinc compound formed at the same time, the solution should be left for several hours, when a considerable portion of this salt will

[10] Relative to bleaching wool with solutions of sodium bisulfite, see *Färber-Zeit.*, 1906, p. 113.

crystallize out. The clear liquor should then be syphoned off, leaving behind the excess of zinc dust and the crystals of zinc-sodium sulfite. To remove all of the zinc compound from the solution, it is necessary to add milk of lime, which will precipitate the zinc in the form of zinc hydrate, leaving calcium and sodium bisulfites in solution with the sodium hydrosulfite. The liquid should be allowed to settle, and the clear supernatant solution run off.[11] The solution is then made up to a bath to stand at about 2° Tw., and the well-scoured wool is soaked therein for 6 to 8 hours in the same manner as when bleaching with solutions of sodium bisulfite. After bleaching, the goods should be thoroughly washed; and, as the same conditions hold as for the bleach with sulfurous acid, if it is necessary to remove all of the sulfur compounds, the wool must be after-treated with oxidizing agents.

For tinting purposes with the sodium hydrosulfite bleach, indigo in small quantity may be added directly to the bleaching liquor, for sodium hydrosulfite readily reduces this coloring matter to the soluble indigo-white which then dyes the wool, and becomes reoxidized to indigo-blue, so that the tinting may be carried out simultaneously with the bleaching.

The water employed for preparing the solution of sodium hydrosulfite, and also that used for diluting the bath, should be boiled for the purpose of removing the dissolved air; as in this manner the efficiency of the bath is much increased, for otherwise the dissolved air in the water rapidly oxidizes the hydrosulfite, and renders it unsuitable for purposes of bleaching. If all of the zinc dust is not removed from the bleaching solutions, the goods will be liable to be stained.

At the present time preparations of sodium hydrosulfite may be obtained in a solid and stable form. One of the earliest of these preparations was Hydrosulfite Conc. of the Badische Co. This consisted of a double hydrosulfite of zinc and sodium in a crystalline form; it was made by preparing crystals of sodium hydrosulfite by the addition of common salt to a concentrated sodium hydrosulfite solution prepared in the usual manner from sodium bisulfite and zinc dust. Zinc hydrosulfite was prepared by the action of zinc on a solution of sulfurous acid. The Hydrosulfite Conc. was mixed with a small amount of alcohol for the purpose of enhancing its keeping qualities. The chief drawback to its use was that when a package of it was opened it had to be quickly used up. Hydrosulfite Z (of the Farbwerke Höchst) is dry zinc hydrosulfite precipitated from solution by the use of sulfuric or hydrochloric acid. This product, however, is but little used except in connection with synthetic indigo. Zündel, in

[11] The following method of preparing a solution of hydrosulfite is given: 8 galls. of sodium bisulfite (72° Tw.) and 19 galls. of water are mixed cold; 7 lbs. of zinc dust made into a paste with a little water are then gradually added, taking care that the temperature does not rise over 95° F. Stir carefully for 10 mins. and then allow to stand for 1 hr. Draw off the clear liquor into milk of lime prepared by cautiously slaking 9 lbs. of burnt lime in 2 galls. of water. Stir slowly for 10 mins. then allow it to settle over night. Draw off the clear solution of hydrosulfite into glass carboys. As the hydrosulfite solution is not very stable it is not advisable to prepare more than a three days' supply. The addition of a little caustic soda (1 gill of caustic soda solution 76° Tw. to 6 galls. of hydrosulfite) will tend to preserve the solution better.

1902, discovered that by the addition of formaldehyde to sodium hydrosulfite it could be obtained in the dry condition and a stable form. This process is being worked by the Farbwerke Höchst and the Cassella Co. The former company put its product on the market under the name of Hydrosulfite NF, while the latter company sold it under the name of Hyraldite A. In the preparation of these products a solution of sodium hydrosulfite is made in the usual manner by the action of zinc dust on a solution of sodium bisulfite; the hydrosulfite is then salted out, filtered and pressed, and then mixed with 25 to 30 percent of formaldehyde, and finally dried in a vacuum. It has been found that a better product is obtained by mixing with zinc oxide. Preparations containing the latter are sold under the names of Hydrosulfite NFW and Hyraldite W. The Badische Co. have also improved their product and sell it under the name of Hydrosulfite BASF.

Since the war several firms have successfully prepared and marketed various hydrosulfite compounds suitable for use in wool bleaching and the stripping of colors. The pure anhydrous sodium hydrosulfite as well as the zinc and formaldehyde compounds can now be obtained of American make and of excellent quality.

5. Bleaching with Peroxides.

Though hydrogen peroxide has been employed to some extent in practical wool bleaching, its high cost excludes it from general application; and the same may be said with regard to barium peroxide from which hydrogen peroxide is made. The recent introduction of improved methods for the preparation of sodium peroxide has led to its manufacture on a large commercial scale, and by its use the peroxide method of bleaching may be carried on within reasonable limits of cost.[12]

Hydrogen peroxide is prepared by treating barium peroxide with an acid, either sulfuric, hydrochloric or even carbonic acid being used for this purpose. Barium peroxide in turn is made by heating barium oxide in a current of air, whereby it absorbs oxygen and becomes converted into the dioxide:

$$BaO + O = BaO_2$$
$$BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4.$$

Hydrogen peroxide has the chemical formula H_2O_2; and in the pure state it is a colorless, oily liquid, easily decomposed into oxygen and water. The commercial hydrogen peroxide is a solution of this substance in water, containing from 3 to 6 percent of actual hydrogen peroxide.[13] The strength, however, is always indicated by the num-

[12] There have been various forms of peroxide bleaching agents suggested for use, all of which eventually depend for their bleaching effect on the action of hydrogen peroxide. These agents are hydrogen peroxide, sodium peroxide, sodium perborate, sodium percarbonate, sodium persulfate and sodium persilicate; the last three, however, have only a theoretical interest to the bleacher. For a discussion of these various bleaching agents see F. Erban, *Färb. Zeit.*, 1909, and O. Kausch, *Elsässer Textilblatt*, 1911 and 1912.

[13] Bohn and Leyden have prepared hydrogen peroxide in the solid form by adding to a solution of hydrogen peroxide a quantity of gelatine and glycerin, and then cooling the mixture until a hard solid mass is obtained. This product is said to remain stable for a long time, and is made active by simply heating to a temperature of 75° to 100° Fahr.

ber of times its volume of oxygen it is capable of liberating; a 10 volume strength, for example, meaning that one liter of the solution will liberate ten liters of available oxygen gas.[14] Some confusion has existed as to the true meaning to be given to the volume strength of hydrogen peroxide solutions; whether it should refer to the volume of available oxygen present in the solution, or to the volume of oxygen which is liberated when the solution is treated with potassium permanganate. It would seem the better practice to have the volume of strength conform with actual volume of available oxygen. Solutions of hydrogen peroxide are usually kept slightly acid, as otherwise they would lose their available oxygen very rapidly; phosphoric acid is mostly used for this purpose. Even with the best precautions, however, solutions of hydrogen peroxide gradually lose their strength, especially in the presence of organic matter or metallic salts.[15]

For the bleaching of woolen goods with hydrogen peroxide a bath is prepared containing 1 gallon of hydrogen peroxide (10 volume strength) and 9 gallons of water. For 100 pounds of woolen cloth approximately 100 gallons of such a solution will be required for satisfactory bleaching.

Suggestions have been made in various patents to bleach with hydrogen peroxide by saturating the goods with a strong solution of 1 part hydrogen peroxide (3 percent) and 1 part of water, squeezing and subjecting to the action of hot ammonia vapors. These methods, however, while more complicated, do not seem to be any more efficient or satisfactory than the usual simple process of steeping the goods in the weak solution of hydrogen peroxide.

Sodium peroxide has the chemical formula Na_2O_2, and it appears in trade in the form of a yellowish white amorphous powder. It is manufactured at the present time on a large scale by the electrolytic method; that is to say, the metallic sodium for its manufacture is made by this method. The peroxide itself is made by heating the metallic sodium contained in aluminium vessels in a current of oxygen gas:

$$Na_2 + O_2 = Na_2O_2$$

The composition of the commercial product is approximately as follows:

	Percent
Sodium peroxide	93.0
Sodium oxide	2.0
Sodium hydrate	2.5
Sodium carbonate	2.5

The samples at first sent into market contained appreciable amounts of iron, but this has been remedied by the use of aluminium retorts, and the sodium peroxide now to be met with is perfectly free from iron. If kept dry, sodium peroxide is quite stable in character, but in the presence of moisture or organic matter it readily decomposes into

[14] Hydrogen peroxide may now be obtained commercially of 24 volumes strength.

[15] According to Wolffenstein, bleach baths of hydrogen peroxide may be best made up in vats made of tin or tin-lined materials (see *Ger. Pat.* 206,566).

caustic soda and oxygen; and under such conditions, it may become quite dangerous in handling, and serious fires and explosions may result; consequently this chemical should be stored with the greatest of care. When thrown into water sodium peroxide dissolves with the evolution of great heat, which causes it to sputter up and take fire, hence much precaution should be taken in dissolving it; it should be sifted gradually into the water and never be added in large lumps; the same precautions should be taken, in fact, as when adding sulfuric acid to water. When dissolved in water, sodium peroxide forms hydrogen peroxide and caustic soda in the following manner:

$$Na_2O_2 + 2\ H_2O = H_2O_2 + 2\ NaOH.$$

As hydrogen peroxide solutions are not very stable in the presence of an alkali, the solution of sodium peroxide will gradually decompose with the liberation of oxygen gas.[16] When the solution is acidulated, however, as when sodium peroxide is dissolved in dilute sulfuric acid, sodium sulfate and hydrogen peroxide are produced, both of which remain in solution together with the excess of acid. This forms a very convenient method of preparing solutions of hydrogen peroxide.

In the peroxide bleaching of wool, more than in any other process of bleaching, it is very essential that the material be thoroughly cleansed, and this is particularly true in the case of cloth. Any residues of fat or soap or particles of iron or rust (from the cards or combs) will cause a rapid decomposition of the peroxide solution. The very ready decomposition of the bleach bath explains the fact that in piece bleaching establishments where only pure and carefully prepared piece goods are treated the bleach baths may be kept running continuously for a month with proper freshening up each day, while in establishments operating on rather impure yarns or on loose wool the bleach baths decompose very rapidly and often spontaneously with effervescence. It may be generally assumed that the less pure is the material to be bleached the more rapid will be the decomposition of the hydrogen peroxide and in consequence the higher will be the cost of the bleaching.

It is also important for success in peroxide bleaching to have a good supply of pure water, which should be as free as possible from organic impurities, and especially free from iron.

Bleaching with sodium peroxide is carried out in the following manner: The bath is prepared by first adding the requisite amount of sulfuric acid to the water, and then cautiously sifting in the required amount of sodium peroxide. The bath is then tested with litmus

[16] In the consideration of peroxide bleaching compounds it has been found that certain peroxide salts possess a greater degree of stability than others. This is especially true in the case of magnesium peroxide, which is much more stable than sodium peroxide, and which according to Prudhomme exists in combination with the hydrate and has the probable formula:

$$3\ Mg\ (OH)_2 + MgO_2 \text{ or } 3\ Mg\ (OH)_2 + MgO\ (OH)_2$$

If, therefore, magnesia or a salt of magnesium such as magnesium sulfate, Epsom salt, etc.), is added to a peroxide bleaching bath, the tendency is to increase its stability, owing to the formation, in part at least, of magnesium peroxide which has a much slower rate of decomposition. Castner (*Ger. Pat.* 74,173) has suggested the use of mixtures of sodium peroxide and magnesium sulfate (or chloride). Calcium salts may also be used, but the stabilizing effect is less.

paper, and if the amounts of acid and peroxide have been properly calculated, the bath should show a slight acid reaction, and turn blue litmus paper red. It is necessary that there should be at least a slight excess of acid in order to insure complete neutralization of the caustic soda formed in the reaction;[17] as if any of this latter compound is left in the solution it may very seriously injure the wool being bleached. The reaction which takes place is as follows:

$$Na_2O_2 + H_2SO_4 = H_2O_2 + Na_2SO_4.$$

It is best to add the chemicals in the order described; that is the acid first and the sodium peroxide last, as in this way there will not be so much loss of oxygen;[18] for if the peroxide is added first and then the acid, there will be so much heat liberated by the peroxide coming in contact with the water, and in the presence of the alkali, the hydrogen peroxide formed will be more likely to decompose, whereas, by assuring a constantly acid liquor for the solution of the hydrogen peroxide as fast as it is formed, there will be less loss of oxygen. If the bath is not to be used directly for bleaching, it should be left in the acid condition; but immediately before use, the bath should be brought to a slightly alkaline condition by the addition of ammonia water; although sodium phospate, borax, magnesia, sodium silicate, or other mild alkali may be used for this purpose.[19] By making the bath alkaline its bleaching action is rendered more rapid; care, however, should be taken not to add too much or too strong an alkali, as then the oxygen would be liberated unnecessarily fast, and the bath would run down too rapidly. After the alkali has been added in sufficient amount to turn red litmus paper blue, the wool is steeped in the bath, and left for 10 to 20 hours; after which it is taken out and washed off with water containing a small amount of oxalic acid. The bleaching bath must be made up in a wooden or cement tank absolutely free from metal parts such as iron, copper, etc. The smallest amount of iron, such as a nail, will render the bath useless, as the oxygen will be rapidly liberated and the iron oxide formed will stain the wool. The use of water containing any trace of iron must also be avoided. In fact, there will be sufficient iron present in water which is delivered through iron pipes for any distance, especially if the water is allowed to stand in the pipes for any length of time, to cause it to be unfit for use in bleaching with sodium peroxide. Water lying in iron pipes over Sunday when used on Monday morning will generally contain enough dissolved iron to ruin the peroxide bleaching bath; and on this account imperfect results are often obtained by the use of this method, and the fault has been hard to locate. It is best to have the iron pipes

[17] For the neutralization of 100 parts of sodium peroxide there is required 133 parts of sulfuric acid of 66° Bé.

[18] Sodium peroxide is now put on the market in the form of compressed tabloids. The object of this is that the tabloids dissolve more slowly in water and cause less loss of oxygen, the peroxide also keeps better in the tabloid form, and when used less of the chemical gets into the air in the form of dust to attack the mucous membranes of the nose and eyes.

[19] In the bleaching of mohair with sodium peroxide, greater care must be exercised than in the treatment of wool with respect to the alkalinity of the bath and its temperature. As far as possible, the bath should be neutral and the temperature should not be higher than 100° F. A bath of one-volume strength is sufficient for the bleaching of mohair.

coated inside with tar paint, as this also renders the water more suitable for purposes of dyeing as well as bleaching. Caution should also be had that the sulfuric acid employed in the preparation of the peroxide bath should be as free from iron as possible. Many unsuccessful attempts at the use of peroxide bleaching can be traced to the use of sulfuric acid containing sufficient iron to destroy the efficiency of the bleach.[20] The bleaching bath should be maintained at a temperature of about 100° to 120° F., and the steam for heating may be introduced by either rubber or lead pipes. The pipe should simply traverse the tank and be open at the exhaust end, in order not to have the steam superheated while passing through the bath. By using a higher temperature in the bath the time for bleaching may be somewhat shortened, but there will also be a large and unnecessary loss of oxygen.

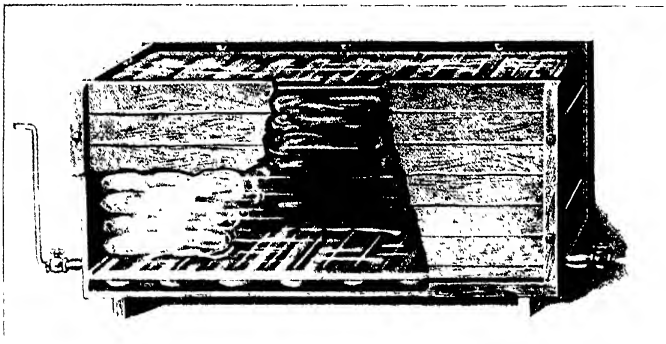

FIG. 77.—Bleaching Vat for Peroxide Method.

In order to tint the bleached wool, it may be washed after coming from the bleaching bath in water slightly acidulated with oxalic acid and containing a trace of Indigo Extract or Acid Violet. The only substance left in the wool after coming from the bleaching bath is sodium sulfate, any excess of which is very readily removed when washed with water; and if any of the salt is left in the goods its presence causes no bad results, except in so far that when present in considerable amount, the salt on drying may show a white efflorescence; but this will very seldom be the case, as the bleaching baths are usually not sufficiently concentrated, and such a result will only happen when the bath is worked continuously and becomes too heavily charged with sodium sulfate. Such an efflorescence, however, is readily removed from the wool by washing in water. Another point in favor of this method of bleaching is that the white so obtained is a permanent one, and the natural yellow tint of the fiber does not return again on washing and exposure to the air, as in the case of bleaching with sulfurous acid.

[20] For effect of different metals on bleaching baths of sodium peroxide, see Luttringhaus *Färber-Zeit.*, 1901, p. 328 and 1902, p. 165.

the substances be used in the proportion of three parts by weight of the magnesium salt to one of the sodium peroxide. The process is operated in the following manner: Thoroughly wet out the wool in a solution containing 30 percent of its weight of magnesium sulfate; then lift the wool, add 10 percent of sodium peroxide; re-enter and raise the temperature to 160° F., maintaining it at that point for one hour, when the process should be complete. On adding the sodium peroxide to the bath the liquid becomes milky, which is due to the insolubility of the magnesium peroxide. A subsequent washing in a dilute acid bath will remove any adhering oxide of magnesium which may have been precipitated on the fiber. The saving in time by this process compared with that by the ordinary one is very great, but the cost is considerably more.[25]

The peroxide bleach is not only useful for goods which are to remain in the white condition, but also for wool which is to be dyed in delicate shades. Wool which has been bleached by the sulfur process cannot be dyed in light tints unless the excess of sulfurous acid has first been removed by a treatment with an oxidizing agent, as the sulfur dioxide if left in the fiber would destroy the great majority of dyes in such tints.

In setting a fresh bath with hydrogen peroxide or sodium peroxide, especially if wooden tubs are used, it is best to first bleach out the tub together with all wooden material to be used in the bleaching, steeping them in a solution of sodium peroxide over night. For this purpose a ½ percent bath may be used; in this manner the coloring matter in the wood, which might otherwise be extracted and stain the goods, is removed. All the chemicals employed in connection with bleaching with sodium peroxide, such as acids, soaps, etc., should be first examined to ascertain if they are free from iron, as otherwise bad results may be obtained. Iron steam- or water-pipes, from which condensed steam may drip down, should not run over the tanks containing the sodium peroxide solution, as iron is liable to be introduced into the bath in this manner.

The question as to whether hydrogen peroxide or sodium peroxide is cheaper for the preparation of the bleach bath has been the subject of much discussion (see *Färber-Zeit.*, 1900, pp. 268, 337, 398; 1903, p. 412; 1904, p. 58). While sodium peroxide is much more concentrated and consequently has less freight charge in transportation, on the other hand, it requires a considerable amount of sulfuric acid for neutralization. The only proper criterion in this matter would be the results obtained in practice on a comparative use of both compounds.

In the tinting of goods bleached by the peroxide method, trouble is

[25] Another formula for bleaching wool or half wool goods by this process, but using a weaker bath and giving a longer treatment, is as follows: Prepare a bath containing 18 percent (on the weight of the goods) of magnesium sulfate (Epsom salts) at 160° F., then add 6 to 8 percent of sodium peroxide dissolved separately. Work the goods in this bath for one hour and then sink under the liquor over night. The goods must be kept below the surface while left lying and this is best done with a wooden grating loaded with clean stones. This grating must be made without iron nails. The bath may be kept standing for weeks, reinforcing for each batch with 4 to 5 percent of sodium peroxide and 12 to 15 percent of magnesium sulfate. At each heating-up of the bath a thick froth forms which must be skimmed off. This froth contains most of the precipitated magnesia.

sometimes experienced in the fact that the tint is not permanent, and washes out. It has recently been claimed, however, that if the goods are blued with Acid Violet or Alkali Blue before bleaching, the tint will be far more permanent.

In bleaching wool by the peroxide method, Koechlin recommends the use of sodium bisulfite in connection with the peroxide in order to increase the efficiency of the bleach. The woolen material is steeped in the peroxide bath, allowed to remain rolled up for a short time, and then passed through a bath containing sodium bisulfite. This treatment not only heightens the effect of the bleach, but also gives the wool a somewhat better luster.

6. The Permanganate Bleach.

Potassium permanganate is a salt of permanganic acid, which is a highly oxidized body. The potassium salt possesses the chemical formula $K_2Mn_2O_8$. Its strong oxidizing action is due to its tendency to decompose, especially in the presence of acids, to form lower oxides of manganese; thus,

$$K_2MnO_8 + 3H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 3H_2O + 5O.$$

That is, one molecule of potassium permanganate is capable of furnishing five available atoms of oxygen for bleaching purposes.

Sodium permanganate can also be employed as an oxidizing agent, though the potassium salt is more to be met with in trade. The disinfecting properties of such liquids as "Condy's fluid" are due to the fact that they contain sodium or potassium permanganates which are capable of rapidly destroying organic matter.

When acid is not present in the decomposition of potassium permanganate, instead of a manganous salt being formed, a brown hydrate of manganese separates out. If acid is not present in the reaction, the decomposition of the permanganate takes place as follows:

$$K_2Mn_2O_8 + 3H_2O = 2KOH + 2MnO_2.H_2O + 3O.$$

The hydrated manganese dioxide is precipitated and the solution becomes alkaline, owing to the formation of potassium hydroxide. Thus, in the bleaching of wool with potassium permanganate, when the material is first worked in a dilute solution of this salt, the fiber rapidly turns brown, and in order to remove the manganese compound it is necessary to subsequently treat the wool with a dilute bath of sodium bisulfite, the effect of which is to reduce the manganese compound to a colorless and soluble salt, which thus being removed by solution leaves the wool in a white condition. The bleaching of wool by this means may be carried out very rapidly, it being necessary to work the material in the solution of potassium permanganate for only a few minutes; after which it is immediately squeezed, and worked in the bath of sodium bisulfite for a few minutes; it is then washed off, and the process is finished.[26]

[26] The use of potassium manganate for the bleaching of wool has also been suggested. The wool is steeped in a solution of 4 percent of potassium manganate and 1 to 2 percent of magnesium sulfate. The latter is said to be added to prevent injury to the fiber by the manganate. After 15 minutes' steeping the wool is removed and treated with a dilute solution of sulfuric acid (or a solution of sodium bisulfate or one of aluminum sulfate may be

The strength of the potassium permanganate solution should be from one to four percent (on the weight of wool) of the salt, and the temperature should not be above 120° F. Too large an amount of permanganate will cause injury to the fiber by excessive oxidation, and it will also be difficult afterwards to completely remove the brown hydrated oxide of manganese. The material after coming from the permanganate bath should not be allowed to stand exposed for any length of time, but should be immediately treated with the solution of sodium bisulfite, otherwise the hydrated oxide of manganese may become so firmly fixed in the wool that it will be difficult to remove except by the use of a large excess of bisulfite; and if too much of the latter is used, it in turn is hard to completely eliminate from the fiber, and the goods will have to be passed through the permanganate bath a second time.[27]

By using a permanganate bath properly acidulated with sulfuric acid, it is said to be possible to prevent the formation of the brown hydrated oxide on the fiber;[28] in which case manganese sulfate is formed simultaneously in the bath. Under such conditions, the second bath of sodium bisulfite may be dispensed with, and only a thorough washing of the wool with water is required.

It has always been claimed that bleaching with potassium permanganate is too expensive for ordinary purposes; but it evidently deserves more attention than it has heretofore received, and if the process is properly carried out, it should not be much more expensive than the method in which sodium peroxide is used, and the time saved should in many cases make it more desirable. The bleach obtained with potassium permanganate is permanent, like the peroxide bleach, for in both cases the coloring matter of the wool is oxidized and absolutely destroyed.[29]

Oxalic acid also has the power to discharge the color on wool due to treatment with potassium permanganate; and instead of after-treating the wool with a solution of sodium bisulfite, it has been suggested to employ solutions of oxalic acid. The oxalic acid reduces the oxide of manganese on the fiber and thus causes its removal in much the same manner as when sodium bisulfite is employed. This method

used) for the purpose of dissolving the precipitated manganese salt from the fiber The sulfuric acid solution is used at a temperature of 20 to 30°C The wool is finally washed and treated with a dilute bath of ammonia. It is doubtful if this process has any practical value.

[27] The following method of bleaching wool with potassium permanganate is taken from practice: For 100 lbs. of well-scoured wool use a bath containing:

4 lbs of potassium permanganate
1½ lbs of magnesium sulfate.

Work the wool in this bath until the solution becomes decolorized, then rinse and enter a weak bisulfite of soda bath acidulated with a small amount of sulfuric acid. This will remove the brown oxide of manganese from the fiber. Rinse the wool again and then repeat the two bleaching operations. Finally wash well in fresh water and soap in a bath containing:

1½ lbs. of soap.
¾ lb. of ammonia.
¼ lb. of glauber salt

[28] In this case about 15 ozs. of sulfuric acid should be added for each 16 ozs. of potassium permanganate used

[29] The permanganate method of bleaching is not so much used on wool itself as it is on such hair fibers as mohair, alpaca, cashmere, etc, for which it serves as an excellent bleaching agent. This process is used chiefly on the material in the form of yarn, rather than on the loose fiber or on cloth.

also has the advantage that there is no objectionable chemical left in the wool, as would be the case with the use of sodium bisulfite, unless there should be just sufficient of the latter employed to neutralize the manganese compound, which is a difficult point to adjust. It has also been suggested to use a bath of hydrogen peroxide after treatment with the permanganate bath. This also causes the decomposition of the manganic oxide, with the additional feature of liberating more oxygen, which should assist in the bleaching of the material.

7. Bleaching with Perborates.

Perborates have recently been introduced as bleaching agents; the chief salt available for this purpose is sodium perborate, though magnesium perborate has also been employed.

Sodium Perborate is a bleaching agent of rather recent introduction. It is sold in the form of a crystalline substance, and contains about 10 percent of active oxygen. In this respect it is somewhat similar to sodium peroxide in that it has a considerable amount of loosely combined oxygen, which under proper circumstances is readily liberated from combination in the nascent state, and thus becomes available for use in bleaching. On dissolving in water, sodium perborate furnishes active hydrogen peroxide and borax in solution, and the latter itself is of some advantage in bleaching, as it has a mild alkaline action and considerable cleansing effect, and, besides, it has not nearly the same destructive action on the fiber as the caustic soda, which is liberated in the use of sodium peroxide. Bleaching with the use of sodium perborate is carried out in practically the same manner as with sodium peroxide.

The relative cost of bleaching with sodium perborate is much too high to permit it to be employed for ordinary purposes of textile bleaching in competition with hydrogen peroxide. Sodium perborate has some vogue for bleaching garments in cleaning establishments and laundries, as it can be used in connection with hot soap liquors without danger of seriously injuring the fabric.

Sodium phosphate is generally employed in connection with the sodium perborate, presumably to increase the alkalinity of the solution without making it caustic, as the bleaching activity (through the formation of hydrogen peroxide) is much greater in an alkaline solution. It is also recommended to treat the material to be bleached to a previous bath of sodium bicarbonate. This also aids to increase the alkalinity of the bleaching solution. This method has been suggested for the bleaching of artificial silk, in which industry it is probably used to some extent, though exact information on this subject is not obtainable.

Sodium percarbonate is also suggested as a bleaching agent similar in its effect to sodium perborate, but there is no indication of its being employed in a practical scale. A number of proprietary bleaching compounds have recently been brought out in Germany chiefly for the purpose of selling for household use, in garment cleaning, bleaching hats, feathers, etc.

Among these compounds is "Clarax," which appears to be a mix-

ture of 20 percent sodium perborate, 25 percent borax, and 55 percent sodium phosphate, though these exact proportions are not always adhered to; "Persil" is a mixture in about the following proportions: 20 percent soap, 33 percent soda ash, 7 percent silicate of soda, 10 percent sodium perborate, and 30 percent water. "Ozonit" is a similar compound containing approximately 38 percent soap, 3 percent silicate of soda, 23 percent soda ash, 26 percent of water, and 10 percent of sodium perborate. Patents have also appeared describing the use of sodium perborate for the bleaching of textiles in a circulating kier, the sodium perborate being mixed with the caustic alkalies employed in boiling-out. It is very doubtful if any of these methods are in practical operation for ordinary purposes of textile bleaching.[30]

[30] According to a recent German patent, stearic acid rapidly and cheaply bleaches defatted wool to a white which is not affected by any subsequent treatment. The stearic acid must be used in the form of an emulsion, which must be acid to litmus. Alkalies, and even the lime in hard water, decreases the bleaching power materially. As regards the emulsification of the stearic acid, that is easily done by the help of a solution of soap or quillaia. It is easy to keep the emulsion acid by adding just a little more stearic acid if required. Any waste emulsion can be utilized by converting it into soap by means of caustic soda or even washing soda.

The following example gives a complete description of the process. An emulsion is made by melting up 30 lbs. of stearic acid in 100 lbs. of hot extract of quillaia, which may be previously mixed with 2 to 5 lbs of a neutral soap, which increases the permanence of the emulsion. To bleach wool with the emulsion, a bath is prepared at a temperature of from 90° to 140° F., containing 1 to 3 gals. of the emulsion per 100 gals. of water. When the goods have been worked in the milky liquid for from 5 to 10 mins cold, they are lifted, wrung to recover the waste bath, rinsed, and dried. The drying should be carefully done. The lower the drying temperature the better the white. Goods bleached this way never turn yellow. The rinsing after bleaching must be thorough, as the emulsion tends to cling to the fiber.

Chapter IX.

Boiling-off or Degumming of Silk.

1. Introduction.

The silk fiber consists of a filament of albuminous matter spun by the silkworm. As the thread, or fiber, issues from the spinneret of the worm, it is in the form of a double filament or fiber surrounded and cemented together by a more or less uniform coating of silk-glue or gum. Outside of the silk-glue there is little or no impurity present on the silk fiber. The silk fiber itself differs very slightly in chemical composition from the surrounding layer of glue, but the latter is soluble in hot solutions of soap, whereas the former is not, and on this reaction is based the general process of scouring silk.

The scouring of silk is generally known under the terms of "boiling-off," "stripping," or "degumming." By a complete degumming of the raw silk the loss in weight will be about 25 to 30 percent. For purposes of manufacture, however, it is not always necessary, or even desirable, to remove all of the silk-glue from the fiber. Depending upon the relative amounts of silk-glue removed, the qualities of silk are classified into

(a) Écru silk, from which only about 2 to 5 percent of the glue has been removed.

(b) Soupled silk, from which 8 to 15 percent of glue has been removed.

(c) Boiled-off silk, from which all the glue has been removed.

2. Nature of the Impurities in Silk.

The silk fiber proper consists of a proteoid substance resembling the proteoid of wool very much in its general properties; it is known as *fibroin*. The silk-glue is a mucilaginous substance known as *sericin*. This latter body is yellowish in color, though the intensity of the coloration varies considerably with the nature of the silk. Most Chinese and Japanese silks have but a small amount of coloring matter in the sericin; whereas in yellow Italian silk the color of the silk-glue becomes a deep yellow. The amount of sericin in raw silk will average about 25 percent, though this figure will vary within rather narrow limits, depending on the variety of the silk fiber; it will probably, however, never fall below 22 percent and never rise above 30 percent. The sericin is hard and brittle and quite translucent, but without much luster; its presence in raw silk causes the fiber to be harsh and stiff, and it is not

until the sericin has been removed that the silk fiber exhibits its characteristic qualities of softness, pliability, and brilliancy.

According to the analysis given by Richardson, sericin has the following chemical composition:

	Percent
Carbon	48.80
Hydrogen	6.23
Oxygen	25.97
Nitrogen	19.00

From this composition its formula has been deduced and is given as $C_{16}H_{25}N_5O_8$. Other authorities have given analyses of sericin, varying somewhat from the above with a corresponding modification of its chemical formula. It is hardly probable, however, that sericin is a simple chemical substance, but may consist of a number of complex bodies, so any chemical formula which may be assigned to it is only a temporary expedient, and only represents the relative proportions of its component elements.

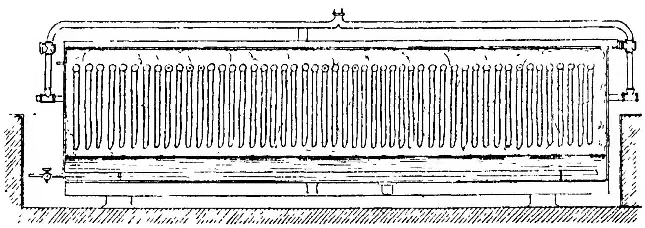

FIG. 78.—Schmid Apparatus for Degumming Silk in Foam Bath.

Sericin is produced in the glands of the silkworm, and is excreted simultaneously with the liquid fibroin. There is some uncertainty on this point, as some authorities assert that the silkworm has no special glands for the secretion of the sericin, but that the worm only secretes one sort of liquid, and that the sericin is only an alteration product of the fibroin produced by the chemical action of the air. This view, however, has many points against it, as it would not account for the very uniform and even differentiation between the layers of fibroin and sericin in the spun cocoon thread. Sericin swells up and softens in cold water, and readily dissolves in hot water, from which solution it gelatinizes on cooling. It is more readily soluble in hot soap solutions and in dilute solutions of caustic alkalies. Strong solutions of caustic alkalies may not be employed for the removal of sericin, as these also dissolve the fibroin of the silk, especially if applied hot; even weak solutions, though they appear to have no solvent action on the fibroin, destroy the luster of the fiber and also discolor it. The carbonate alkalies act very much in the same manner as the caustic alkalies, though less energetically. Neutral soap solutions, however, even when employed at a boiling temperature, do not seem to attack the fibroin, while they completely dissolve the sericin, on which account

strong soap solutions are almost exclusively employed for the boiling-off of silk.

Pure sericin may be prepared by boiling raw silk in water for several hours, and then precipitating the crude sericin solutions by the addition of acetic acid of one percent strength. The separated sericin is washed by repeated decantations with water, then treated with cold, and finally with boiling alcohol, after which it is extracted with ether.

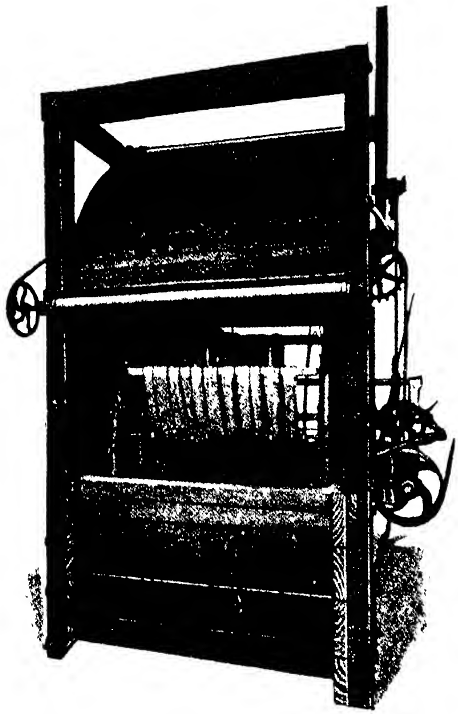

FIG. 79.—Machine for Degumming Silk in Skeins (Klauder-Weldon).

Like other glue-like substances, sericin is coagulated and rendered insoluble in water by a treatment with formaldehyde; consequently, by treating raw silk with this reagent the coating of silk-glue may, to a considerable extent, be retained when desirable.

Besides sericin, mulberry silk also contains a small amount of fats and waxes which are likewise removed by treatment with soap solutions. Richardson gives the following composition to mulberry silk:

	Percent
Water	12.50
Fats	0.14
Resins	0.56
Sericin	22.58
Fibroin	63.10
Mineral matter	1.12

Silberman gives some analyses which are very similar to the above, as follows:

	White Raw Silk Percent	Yellow Raw Silk Percent
Fibroin	73.20	72.35
Sericin	22.28	23.13
Wax and fat	3.02	2.75
Salts	1.60	1.60

These analyses are based on the dried fiber.

The amount of mineral matter in silk will vary considerably with the origin of the silk; in raw mulberry silk it will average about one percent, whereas in boiled-off silk it will average about one-half this, showing that only a portion of the mineral matter is present in the sericin or is removed along with the latter substance. In wild silks the amount of mineral matter is much larger than in cultivated mulberry silk; in yamamai silk, for instance, it reaches as high as 8 percent.

3. Natural Coloring Matter in Silk.

The amount of natural coloring matter to be met with in mulberry silk is very small, and for most purposes may be neglected. The external layer of sericin appears to contain more coloring matter than the boiled-off fibroin, which is usually very white in color, although the raw silk in the gum may have shown quite a distinct yellow or brownish color. The small amount of pigment matter which is to be found in silk is of a yellow color; and, according to Dubois, it is similar in nature to carotin, a vegetable coloring matter. He succeeded in obtaining from it five different bodies, as follows:

(a) A golden yellow coloring matter, soluble in potassium carbonate and reprecipitated by the addition of acetic acid;

(b) Crystals which appear yellowish red by transmitted light and brown by reflected light;

(c) A lemon colored amorphous body, the alcoholic solution of which on evaporation gave granular masses;

(d) Yellow octahedral crystals resembling sulfur in appearance;

(e) A dark bluish green pigment in minute quantities and probably crystalline.

The different varieties of wild silk nearly all possess a more or less pronounced and distinctive color, which is not only present in the sericin, but also impregnates the fibroin or fiber proper, so that the silk does not come up white on boiling-off. This color, in fact, is one of the chief drawbacks to the use of tussah silk, as it is furthermore quite difficult to remove by bleaching. Tussah silk also contains a consider-

able amount of lime compounds, which, by combining with the soap and forming insoluble products, introduces difficulties in the way of boiling-off this silk. In fact, it is usually necessary to remove the lime from the fiber before soaping by a preliminary treatment with a dilute solu-

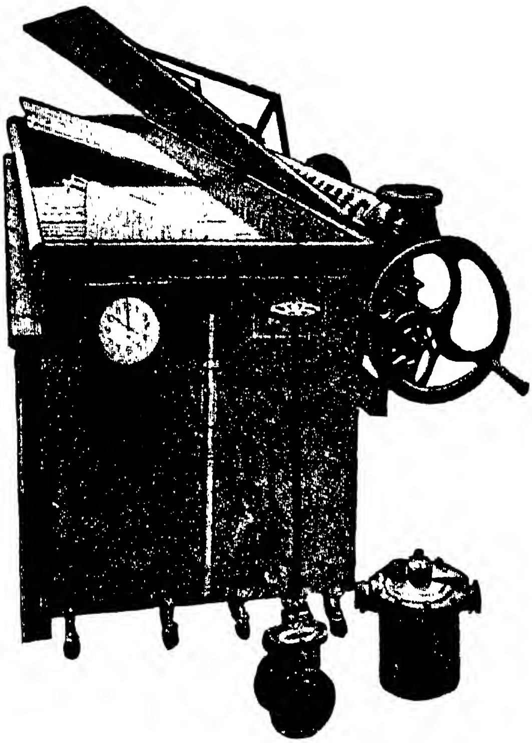

Fig. 80.—Degumming Machine for Silk Skeins.

tion of hydrochloric acid. The amount of lime, together with magnesia, which acts in the same manner, present in tussah silk is about one percent, while the total amount of mineral matters usually to be found in this silk average about 5.5 percent.

4. Stripping Silk with Soap Solutions.

The general method employed for the removal of the gum from raw silk is to boil the fiber in a rather concentrated solution of a good neutral soap. To remove all of the gum the time of boiling has to be considerably prolonged, and the boiling-off has to be repeated several times in fresh solutions of soap.

The strength of the soap bath and the number of scouring baths

through which the silk is passed will depend upon the amount of silk-gum to be removed. In the preparation of the scouring bath sufficient water must be used to permit the silk skeins to hang freely and without too much crowding so that the material may be readily worked in the solution. Experience has shown that 10 pounds of silk will require at least 10 to 12 gallons (U. S.) of water. The usual strength of the scouring bath will contain about 3 pounds of good olive oil soap for this amount of water. The temperature of the bath is usually maintained somewhat under the actual point of boiling in order to prevent the tangling of the silk. At first the silk fiber swells up and becomes sticky, but in a short time the gum begins to dissolve and the underlying glossy fiber becomes apparent. After the required degree of boiling-off has been reached the silk skeins are squeezed and rinsed in water containing a small quantity of soap, about four ounces, and soda ash, about two ounces, per gallon.

The soap used in the boiling-off of silk should also be carefully selected. It is necessary that such a soap be free from caustic alkali, as even small amounts under such conditions would produce a bad effect on the silk, either partially dissolving it or destroying its luster. Soda soaps made from olive oil, tallow, or olein are probably the best soaps to be used for stripping silk; tallow soap is not as good as the other two, for it does not wash out with as much readiness. Cotton-seed oil soap is objectionable on account of its liability to leave a bad odor in the silk. It is better to use a soda than a potash soap, principally due to the fact that the latter is more liable to contain considerable quantities of free caustic alkali. Sometimes small amounts of potassium carbonate are used together with the soap in the stripping bath in order to increase the alkalinity of the soap; it is doubtful, however, if this practice is a beneficial one.

Cocoanut oil soap has sometimes been recommended as proper for use in the boiling-off of silk; the only point in its favor, however, is that it is not decomposed by hard water with the formation of lime soaps. Its disadvantages are its alkalinity and the bad smell that is left on the goods. The use of an excess of caustic alkali is almost inevitable in the preparation of a thoroughly saponified cocoanut oil soap, and this makes it unsuitable for the degumming of silk. Tallow soap rinses out with more difficulty than either olive oil or olein soap, the latter indeed being the best in this respect. Cotton-seed olein is said not to be so good, as it is liable to leave an objectionable odor on the goods. In the more recent methods of purification of cotton-seed olein, however, this objectionable feature has been practically entirely overcome. Though theoretically a perfectly neutral soap would seem the best for stripping and boiling-off, it is found in practice that a soap made slightly alkaline with potassium carbonate gives on the whole somewhat better results; though in this connection it should be thoroughly understood that any alkalinity arising from caustic potash or caustic soda is deleterious to the silk, making it dull in appearance and harsh to the feel.

In the boiling-off of silk various attempts have been made to replace the expensive soap baths with other materials, but the results are never

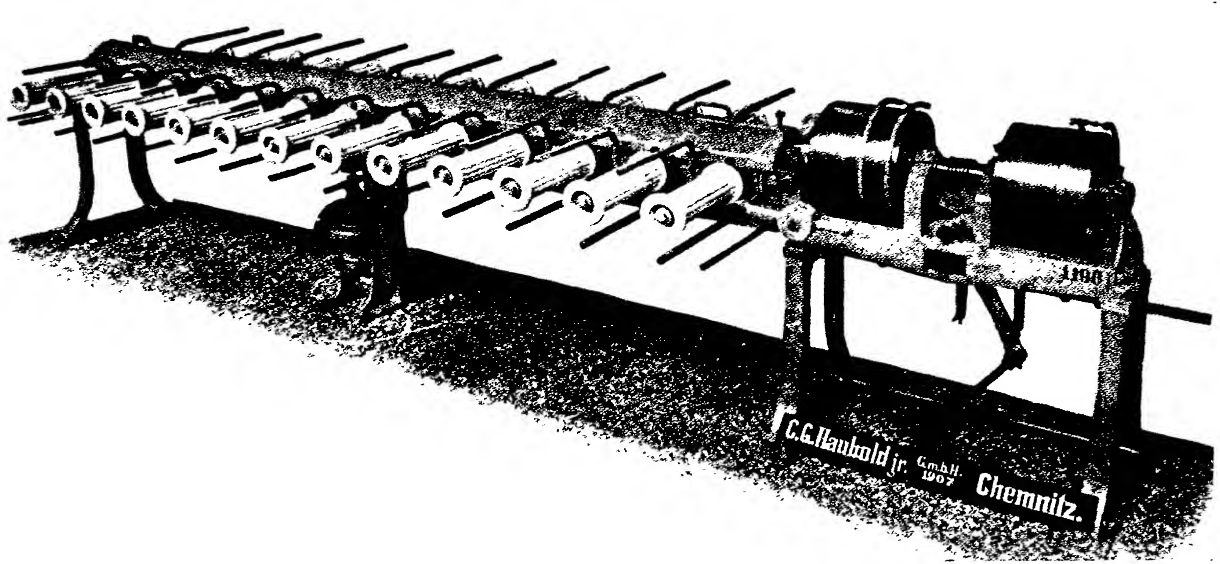

Fig. 81.—Skein Washing Machine with Porcelain Rolls.

as good and the quality of the fiber is liable to be injured to an extent which will cause more of a loss in value than that gained by the use of cheaper materials than soap. For the boiling-off of silk waste in mechanical apparatus it has been found possible to get good results with the use of sodium sulfide with the addition of glycerin, grape sugar or gelatine (see *Zeit. Farben-Ind.*, 1904, p. 306).

5. Foam Method of Stripping.

A rather recently developed process for boiling-off or degumming of silk is that proposed by Schmid, of Basle, in which the soap bath is replaced by one of soap foam.[1] In this process the silk skeins are hung in the upper part of a vessel on rotating arms in such a manner that they do not come in contact with the soap liquor in the bottom of the vessel, but only with the foam which is constantly rising from the liquor.[2] It is also claimed that the process may be somewhat shortened by the addition of sodium phosphate or acetate to the soap liquor to increase its conductivity for the passage of an electric current which is sent through it (see *Ger. Pat.* 196, 571). Also, by treatment of the silk with formaldehyde the layer of silk-glue may be hardened in any desired manner, as for the preparation of écru or souple silk, so that the silk-glue will not be materially removed in subsequent dyeing operations.[3] The degumming by the foam method has attracted considerable attention in Europe, and apparently the process has met with commercial success.[4] Reports on the process indicate that the strength, elasticity and dyeing properties of the silk are the same as with the old process; the silk is completely freed from gum, while the loss in weight is somewhat less; the luster and handle are said to be better, while there is less evidence of splitting of the fiber.

According to Colombo and Baroni, who have compared the foam process with that ordinarily used, the following facts may be stated in regard to this process:

(1) The froth method extracts the silk-glue from raw silk as completely as the process of a boiling in a soap solution, but the silk loses less weight as a small amount of the soap solution remains in the fiber;

(2) The process is completed more quickly with the foam method;

(3) The influence of hard water is no greater in the new process than in the old one;

(4) If the silk has been treated with soaps, fatty substances or other agents to facilitate the working of the fiber and subsequently conditioned, the foam method is not as efficient;

(5) The strength and the elasticity of the fiber and its behavior towards weighting and dyeing materials are the same in both processes;

(6) The foam method of degumming leaves the fiber in a better condition with respect to handle and luster, and the fibers being less agitated are in a better condition for subsequent handling.

[1] *Jahres Berichte*, 1906, p. 383.
[2] *Ger. Pat.* 179,229.
[3] *Ger Pat.* 207,133; also *Färber-Zeit*, 1908, p. 151, and *Jahres Berichte*, 1909, p. 385.
[4] See Colombo and Baroni, *Rev. Gen. Mat. Col.*, 1911, p. 342; *Zeit. angew. Chem.*, 1912, p. 1544; and *Färber-Zeit.*, 1911, p. 493.

According to the Schmid process, raw silk may be simultaneously degummed and dyed by treatment with a soap lather containing a dye-stuff. The following treatment is recommended: For 100 pounds of raw silk, use 58 gallons of water in which 3½ pounds of soap and, as for example, ½ pound of Rhodamine have been dissolved. The silk skeins are suspended or laid in suitable holders in such a manner that the liquid in the vessel may not come in contact with them. The soapy

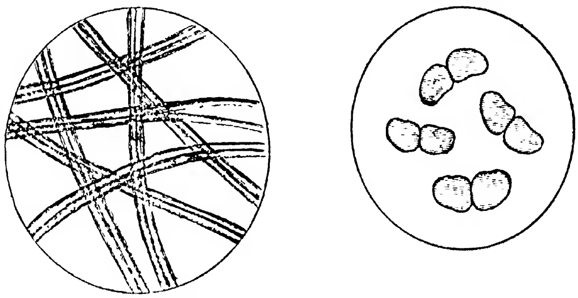

FIG. 82.—Micrograph of Raw Silk and Cross-sections of Fiber.

dye-bath is then heated to the boiling point by means of a closed steam coil so that the liquor is converted into lather. This rises in the vessel and impregnates the skeins of silk, which are thus subjected to the combined action of steam, hot air and the soapy dye lather. The effect of this is to soften the sericin or silk-glue so that the dyestuff will completely penetrate the silk. The skeins are then removed and washed with hot water, which will remove the softened silk-glue. Weighting substances may also be added during the degumming and dyeing process.[5]

6. Defects in Stripping.

The tangling and fraying of silk threads in the boiling-off operation is a defect which should be carefully watched and corrected, as other-

FIG. 83.—Silk Moth.

wise great damage will result. Girard is of the opinion that this defect is due to purely mechanical causes, being the natural result of the agitation produced by the boiling of the soap or by the movement given

[5] *U. S. Pat.* 836,464.

to the material in the bath. This unfavorable effect is greatly aggravated by the following circumstances: At the beginning of the boiling-off operation the silk-glue begins to swell and soften before it dissolves. At this time the filaments of the silk fiber proper are enveloped in a viscous mass, in which they slip with surprising facility. The slightest movement, whether of the solution or of the fiber, is sufficient to change the relative positions of the filaments. If the material is in the form of loose hanks or skeins, the danger is really less, because the tangling of the threads, if not too bad, can usually be corrected by suitable handling and manipulation, but in loose fabrics this displacement of the threads often causes a fraying which in net fabrics, such as tulle and lace, is often incurable. This pasty condition of the silk-glue lasts but a short time, and then it liquefies and becomes entirely dissolved. The silk filaments then come in contact with one another, and in this condition it is very difficult to displace them.

7. Écru Silk.

Écru silk is simply scoured in a weak soap solution, and the endeavor is principally to remove only the small amount of fatty and waxy matters present in the silk without any appreciable loss of sericin, so that the silk may afterwards be dyed. The loss is weight in silk of this character is about 2 to 5 percent. Écru silk resembles raw silk very much in appearance and feel; it is dyed just after scouring, so that the gum may not harden again before the dyestuff has a chance to penetrate into the fiber. Écru silk is largely employed for warps, as it stands the friction of the shuttle well on account of its harsh nature.

Silk is sometimes scoured when in the piece; that is, the yarn may only be soupled slightly, as in the preparation of écru silk, and woven into the piece. This is more especially the case with satins, where a mixture of silk and cotton yarns is used. The methods of scouring such silk are the same as for yarn.

Since écru or hard silk still contains most of the silk-glue, it will also still have practically all of the natural coloring matter which has already been stated as being contained almost entirely in the gum. In order to bleach this kind of silk for white or for the dyeing of bright colors it is sulfured. Owing to the character of this bleach the color is very liable to return after a time. A process for the preparation of white écru silk from the raw yellow silk is to wash in a cold soap bath, rinse, sulfur twice, bleach in *aqua regia*, rinse, treat in a bath of dilute solution of soda ash, then wash again in a weak cold soap bath, rinse, sulfur twice again, and finally rinse.

Hurst gives the following processes for écru silk:

(a) Washing in cold water;
(b) Washing in a 10 percent solution of soap at 80 to 90° F.;
(c) Sulfuring;
(d) Bleaching with *aqua regia;*
(e) Washing;
(f) Sulfuring.

For a very white écru silk the following operations are recommended:

(a) Cold 10 percent soap solution;
(b) Washing;
(c) Sulfuring;
(d) Bleaching;
(e) Washing;
(f) Soaping with 10 percent soap solution at 80 to 90° F.;
(g) Sulfuring;
(h) Washing;
(i) Cold soda ash solution (1½ percent);
(j) Warm soap solution (3 percent);
(k) Washing;
(l) Sulfuring;
(m) Washing.

If the silk is to be dyed in dark colors or black the bleaching and sulfuring operations may be omitted.

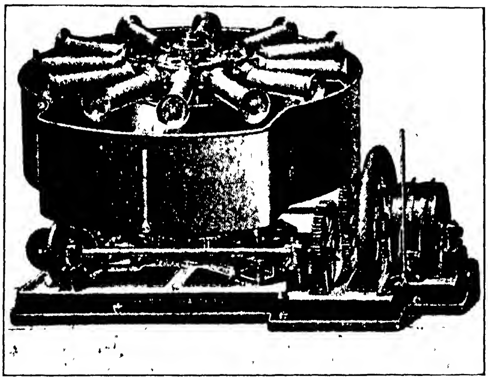

FIG. 84—Circular Machine for Washing Silk Skeins

For écru silk from raw yellow silk, Knecht gives the following process: Boil-out twice with hot water, stove twice in the sulfur chamber, wash and stove again two or three times. If the silk is intended for white the following further treatments will be necessary: Wash cold with soap (1 pound of soap to 10 pounds of silk), rinse, stove twice, bleach with *aqua regia* or nitrose (nitrosyl-sulfuric acid), rinse, treat in weak soda (2 ounces of soda to 10 pounds of silk), turn in a soap bath (4 ounces of soap to 10 pounds of silk), stove twice, and rinse in either pure water or in water slightly acidulated with sulfuric acid.

In order to prevent the removal of too much silk-gum from écru silk it has been suggested to treat the fiber with a solution of formaldehyde (¼ to ½ percent) for several hours, and then pass through a bath of dilute ammonia in order to remove traces of formaldehyde. The sericin layer of silk that is thus treated is said to be insoluble in the

ordinary dilute acid, alkaline and soap baths, and furthermore the fiber is much strengthened by the treatment. This process is that of Ris-Kummer [6] and is said to be fairly successful. It depends on the action of the formaldehyde making the silk-glue insoluble in the same manner as formaldehyde reacts with gelatine. The advantage of this reaction may also be taken in other ways in the treatment of silk. One example of this is to use the process to restore some of the weight lost in the process of boiling-off which gives a greater luster to the finished article than would be possible if only part of the gum were removed. It may furthermore be remarked that gelatine in this connection is somewhat cheaper than silk-glue. The process consists in steeping the silk for an

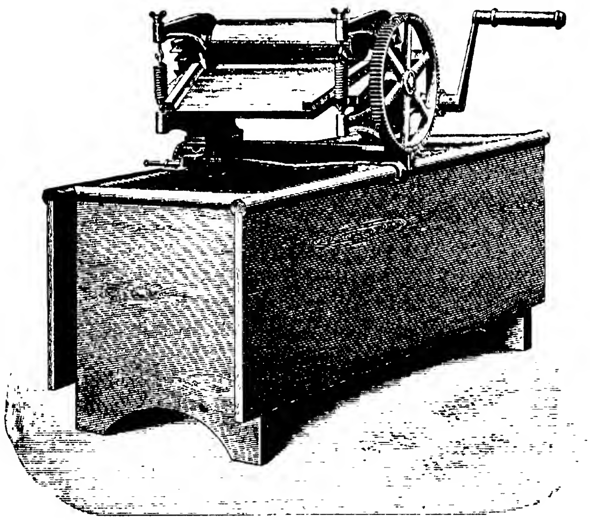

FIG. 85.—Squeezer for Silk Skeins.

hour in a bath containing 20 grams of gelatine per liter at 100 to 120° F., squeezing, gently drying, and then steeping in a bath containing 20 c.c. of formaldehyde per liter. The gelatine is absorbed by the silk in the first bath, and this is later rendered insoluble in the second bath. The treated silk is stiffer than the untreated silk but is fairly brilliant. This process does not interfere with the subsequent dyeing of the silk, which may take place with either basic or acid dyestuffs in the same manner as if the silk had not been treated. The amount of weighting and the stiffness of the finished goods may easily be regulated by using weak or strong solutions of gelatine. In this connection it should be noted that only the clearest and purest gelatine should be used for this purpose if the best results are to be obtained. There are some silk fabrics, such as crêpe, which are not boiled-off before dyeing,

[6] *Brit. Pat.* 15,152 of 1895.

and if it is desired to keep as much of the original gum as possible, this method of Ris-Kummer may be used. Sarcenet silks could also be treated with formaldehyde in the same manner with advantage. Veil silks and net silks may also be treated in this manner to give a stiff waterproof finish.

8. **Soupled Silk.**

In the soupling of silk the raw silk loses from 5 to 10 percent in weight, while the fiber becomes softened sufficiently for purposes of weaving. The raw silk is treated in a weak bath of soda ash and then in a bath containing 4 percent of tartar, 1 percent of sulfuric acid and 15 percent of aqueous sulfurous acid (on the weight of the silk), the temperature of the bath being from 140 to 180° F. The silk is then rinsed, first in warm and then in cold water, until quite free from acid. Silk may also be soupled by treatment in a 10 percent soap bath for 1 to 2 hours at a temperature of 80° F.

According to Hurst, the soupling of silk implies four operations:

(a) *Scouring*, the object of which is to remove the grease and a part of the gum. The silk is treated for 1 to 2 hours in a bath of 10 percent of soap at a temperature of 85 to 95° F.; it is then squeezed and rinsed;

(b) *Bleaching*, which is done with a mixture of 1 part of nitric acid and 5 parts of hydrochloric acid and diluted with water to 5 to 6° Tw. (usually 1 part of mixed acid to 15 parts of water is used). The silk is steeped in this acid bath for 15 minutes and is then well washed and squeezed;

(c) *Sulfuring*, which is done in the same manner as practised in the bleaching of wool. After this process the fiber will have a harsh feel which is removed by softening:

(d) *Softening*, for which purpose the silk is boiled in a weak bath of cream of tartar (½ pound to 10 gallons of water) for 1 to 1½ hours, then squeezed and dried. Just how the tartar acts is not known, and other bodies such as Epsom salts and glauber salt have been tried with some success, but the results are not as good as with tartar.

Soupled silk is not as strong as boiled-off silk, notwithstanding the fact that less gum is removed. It is used principally for filling yarn. It may be dyed in acid baths without any special precautions, but if dyed in soap baths the temperature should be kept down below 140° F. as at higher temperatures some of the silk-gum will be removed and the silk will suffer a loss in weight. If soupled silk is to be used for dyeing in black or dark colors the bleaching and sulfuring operations may be omitted, in which case the silk is simply scoured with soap and then soupled with tartar.

Soupled silk, also known as *mi-cuite* or *mezzo-cotto*, is fuller and more voluminous in fiber than the boiled-off silk. On this account it is particularly serviceable as filling yarn for fabrics where it does not

show on the face side. It is not so much used as a warp thread on account of its lack of elasticity. As it is highly absorbent of tannins and metallic salts it may readily be heavily weighted, owing to the presence of the chemically active silk-gum and the comparatively large volume of porous fiber.

9. Boiled-off Silk.

This is also known as *cuite,* and is fully scoured silk, practically all of the silk-gum having been removed. In this process the silk loses from 25 to 30 percent in weight. Usually two baths are employed for the complete boiling-off of silk, the first containing 30 to 35 percent of soap (on the weight of the silk), and the second about one half of

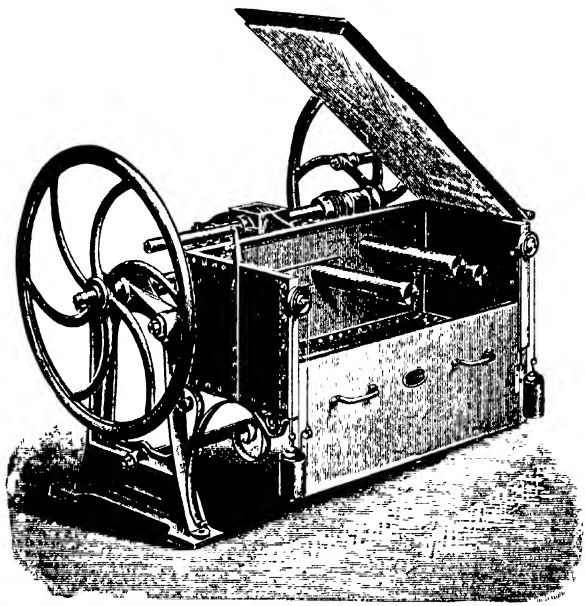

FIG. 86.—Lustering Machine for Silk Skeins.

this quantity. The amount of water used in the scouring bath is about 10 times the weight of the silk; a 100 pound lot of silk will require a bath of about 120 gallons of water and 35 pounds of olive oil soap. The temperature should be kept at 195 to 205° F. The soap baths should be used just at the boil, though not actually bubbling, and the time of treatment is from 1 to 3 hours. Only the purest variety of olive oil neutral soaps should be used for the preparation of the scouring bath. If the silk is in the form of skeins these are often placed in linen bags in order to prevent tangling. In boiling-off, white Japan grêge will lose about 17 percent in weight, while yellow China organzine

will lose about 27 percent. Immediately after scouring the silk should be rinsed free from soap. After boiling-off, the silk is washed first in water containing a small amount of soap and soda ash, and finally in fresh water. The use of the first rinse in an alkaline water is principally for the purpose of preventing any of the soap from being precipitated in the silk. If allowed to stand for any length of time before rinsing, the soap residues are liable to dry into the fiber and they then become very difficult to remove properly, and this will subsequently give great trouble in dyeing and finishing. For the complete removal of the silk-gum from the fiber it is generally necessary to boil-off in three soap baths. Usually these baths are employed in rotation for different lots of silk. On a basis for a bath for 10 pounds of silk, the first scouring liquors should contain about 2½ to 3½ pounds of soap, the second bath about 1½ pounds, and the third bath about 1 pound. After using the last soap bath once, ½ pound of soap is added and then the liquor is used as the second bath; and in the same way, after the second bath has been used there is added 1 pound more of soap, and the liquor is then used for the first bath. This method of operation not only economizes soap but also gives better results. A soap bath may be employed in this manner about three times, but the last scouring solution should always be a freshly prepared one to thoroughly cleanse the fiber.

10. Various Methods of Degumming.

A process of degumming silk by means of steaming is described by Hurst as follows: The skeins of silk are hung on wooden rods in a 30 percent soap bath at a temperature of 150° F. and are worked in this solution until thoroughly impregnated with the soap liquor. The skeins are then hung in a large box which can be closed hermetically and are steamed therein for 20 to 30 minutes at a pressure of 7 to 8 pounds. Silk-gum under this treatment dissolves and runs off the silk into a cavity at the bottom of the steaming box. The silk is next boiled in a weak soap bath for 20 minutes to remove any residual silk-gum, after which it is well washed in soda, squeezed and dried. It is doubtful if this process, however, is of practical value as the color and luster of the silk are liable to be affected by the steaming and saturating with the soap liquor.

According to the Badische Co.[7] silk, also silk-cotton or silk-wool fabrics, may be degummed by treatment with a caustic soda solution containing glycerin or grape sugar. It is claimed that the strength and elasticity of silk degummed in this manner shows no greater loss than with the ordinary soap process; the fiber, however, is not as white and lustrous, but is sufficiently so for silk-wool fabrics, or for material which is to be dyed.[8] The Bayer Co. also recommends the use of caustic soda solution of 36° Bé. with the addition of glycerin for increasing the strength of the silk and its affinity for dyestuffs.[9]

Silk is sometimes weighted in the gum, and in this form usually

[7] See *Ger. Pat.* 110,633.
[8] See also *Ger. Pats.* 117,249 and 129,451.
[9] See *Ger. Pat.* 113,265.

gives considerable trouble in the boiling-off. The metallic compounds employed as weighting materials combine with the soap and give highly insoluble metallic soaps, which are deposited within the fiber and are extremely difficult to remove. The presence of these bodies gives the fiber a sticky feel and dulls the luster. Before boiling-off silk of this character it should first be soaked in water and then steeped in a warm bath (100 to 120° F.) of dilute hydrochloric acid (1 part of acid and 1 part of water) which will dissolve out a considerable part of the min-

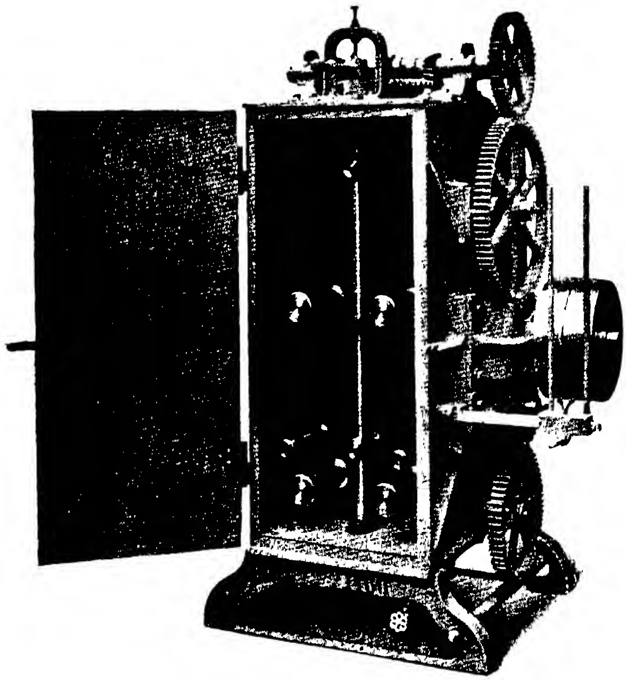

FIG. 87.—Vertical Hank Stretching Machine for Silk Skeins.

eral matter. After steeping in the acid bath for 2 hours the silk is well rinsed in fresh water and is then ready to be boiled-off in the usual manner.

It has also been stated that many silks contain a small amount of lime in the layer of silk-glue, and in the proper treatment of such raw silk for boiling-off it is first necessary to steep for a short time in a dilute solution of hydrochloric acid in order to dissolve out the lime, after which the goods are thoroughly washed and then treated in a bath of dilute soda ash solution for the purpose of completely neutralizing all excess of the acid. This, however, appears to be a rather dangerous treatment, for if any residues of hydrochloric acid are left by any

chance in the silk, it will without doubt produce a rotting of the fiber.

According to Stirm[10] the preparation of completely boiled-off silk (meaning fiber from which all the silk-glue has been removed) involves two operations: (1) A degumming process in hot (210° F.) soap baths, and (2) boiling-off or purging. Between the two operations the silk skeins are frequently stretched, since the degumming process tends to crinkle up the fiber, which by proper stretching is suitably lengthened out and given an improved luster. For the boiling-off or purging process the silk skeins are carefully bundled together in hemp or linen sacks, and, according to the quality of the fiber, boiled

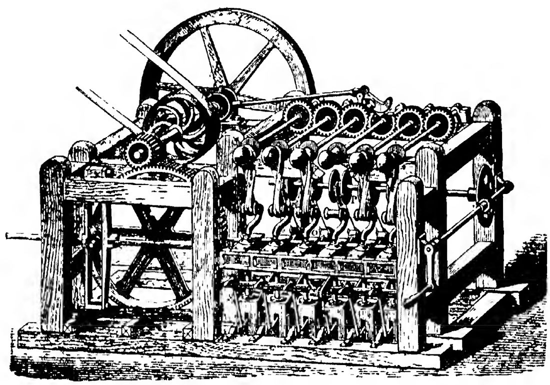

FIG. 38.—Shaking-out Machine (Chevillir) for Silk Skeins.

for ½ to 3 hours with a solution containing 12 to 15 percent of soap (on the weight of the silk). The goods are then rinsed, first with a dilute solution of soda ash and then in fresh water; then hydro-extracted or squeezed and dried. The boiling-off soap bath, after being freshened with additional quantities of soap (it being customary to raise the strength to about 30 percent on the weight of the silk) is used for degumming. According to the origin and quality of the raw silk it will lose in degumming 15 to 20 percent in weight, and in the boil-off an additional 4 to 8 percent, making the total loss 20 to 25 percent, or at times even a little more.[11]

11. Microscopy of Raw and Boiled-off Silk Fibers.

The microscopical appearance of raw silk in the gum and completely boiled-off silk is quite different. In the former case the fibers appear mostly as pairs (the double cocoon filament) cemented together with the silk-glue; also irregular shreds of the glue will be seen adhering to the fibers, and peculiar cross-marks will be seen where one set of fibers has crossed over another and left an impression imbedded in the

[10] *Die Gespinstfasern*, p. 227.

[11] For tables showing the loss of different silks on degumming, see Silbermann, *Die Seide* vol. 2, p. 249.

layer of silk-glue. In the boiled-off silk the fibers appear as single isolated filaments and there is little or no evidence of shreds of silk-glue. The fibers appear as smooth structureless rods of a glassy nature. Sometimes fine hair-like fibrillæ are to be seen resulting from a splitting of the main fiber, and at times the otherwise rounded fiber shows flattened places due to the imprint left by the crossing of another fiber when in the gum.

12. Degumming of Piece Goods.

Though silk is nearly always degummed in the form of skein yarn, there are sometimes occasions when silk in the gum is employed for weaving, and the degumming operation takes place in the piece. The process is practically the same as that used for the degumming of skein yarn, except suitable machines must be employed for handling the pieces. The usual form of washer provided with a revolving winch is a good apparatus for this purpose; also a suitable jigger may be used.

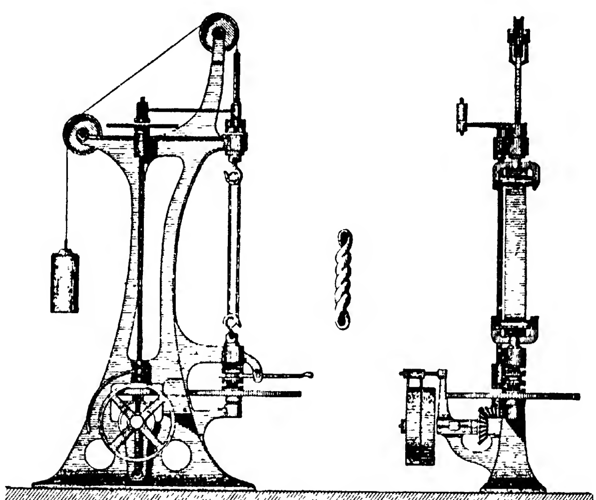

Fig. 89.—Later Form of Shaking-out Machine.

Fabrics containing wool and silk yarns frequently require a degumming of the silk. Such goods are generally singed, crabbed, steamed and then degummed in a bath of soap and soda ash, using a jigger as the machine in order to avoid creases and folds. When soda is used in the bath the temperature should not be run over 140 to 150° F. or the wool will be seriously injured. If soap only is used, a higher temperature may be employed, though as low a temperature as possible is to be recommended if all injury to the wool is to be avoided. Another process for degumming the silk in fabrics containing wool and silk is

to treat first the material with dilute hydrochloric acid, then wash and treat with a soap liquor for several hours at 180° F., after which the goods are rinsed, soaped slightly again and steamed.

Fabrics containing cotton and silk yarns, such as satins, etc., may be degummed in practically the same manner as those consisting of pure silk, as the soap and alkali have no bad effect on the cotton fiber even at a boiling temperature. Sometimes fabrics for dyeing are made from yarns of cotton and silk in the gum and these goods are first weighted by treating with tannin and then with stannic chloride. The pieces are then boiled-off in a soap bath. By this treatment the silk is weighted, and at the same time the cotton is mordanted for dyeing with the basic colors.

13. Boiling-off Silk Waste.

The waste accumulating in silk throwing and known as throwsters' waste consists of silk in the gum. This is used for the preparation of spun silk, but has first to be boiled-off to render it suitable for spinning. A large quantity of waste from silk-reeling is also employed in the same manner, and must be subjected to a similar boiling-off process. The silk waste is first well opened up so as to permit of easy penetration of the liquor and is then put into strong bags of net with a comparatively large open mesh; each bag holds about three-quarters pound of silk and must be packed quite loosely as the silk swells up. The boiling-out vats are of wood, about 6 feet in depth and 4 to 5 feet in diameter, provided with perforated false bottoms under which is placed a closed steam coil. About 2 feet of soft water is run into the vat and then 10 to 15 pounds of white olive oil curd soap in fine shavings are boiled up until thoroughly dissolved, when the temperature is lowered to 180° F. The bags of silk waste are then placed in this soap bath, at first being pushed under the liquor with a pole until they become thoroughly wet-out when they will sink. If the silk wastes are very dusty and dirty it is a very good practice to give a preliminary washing, before the first bath, in a bath of warm water containing a little ammonia, as this clears off the grease and dirt and gives the silk a good white color. The liquor should then just cover the silk, and the steam is turned on, and the material boiled gently. Violent boiling must be avoided as it injures the silk. As the boiling proceeds the bags are constantly turned over in order that the silk may be evenly freed from the gum. After boiling for two hours, the liquor is run off and the silk is hydro-extracted. If time is no consideration, the silk instead of being put into bags is placed loose into the first bath and kept there without movement for 6 to 10 hours at 180° F. so that the gum becomes suitably softened. The silk is then squeezed out and put into the second bath and given the usual boiling. A second boiling is then given in a second vat prepared as before, after which the silk is again hydro-extracted. Should a very white color be desired on the silk, a very small quantity of blue tint may be added to the second bath, which will neutralize the natural creamy shade of the silk. The bags are then opened and the loose silk is rinsed in clean water at 180° F. After

hydro-extracting, the loose silk is well opened up and then dried in a suitable drying machine.

Pentecost[12] states that much of the spun silk prepared from waste silk is tinted before being spun with blue or other coloring matter. It may also be weighted with sugar or other bodies, both for the purpose of fraudulently increasing the apparent weight of the fiber and also to give the thread more body. Under such circumstances, it must be borne in mind that although spun silk has already been degummed in the loose state previous to being spun, nevertheless the spun yarn may still contain extraneous matters which it may be desirable to remove in the process of manufacture, and this may be done either in the state of skein yarn or in the form of the woven fabric. If these added materials are not first removed difficulties and defects may be experienced

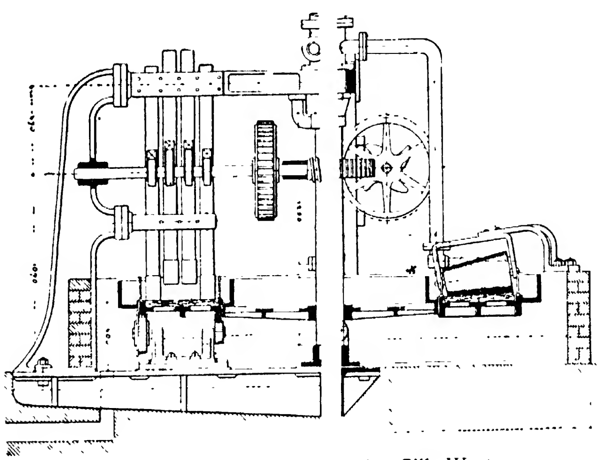

FIG. 90.- Washing Machine for Silk Waste.

in the dyeing or bleaching of the spun silk. It is therefore recommended that all spun silk be tested before dyeing or bleaching to determine if it is pure or not. This may easily be done by scouring a small skein of the silk in a warm dilute soap solution and observing if any material is removed from the silk. It will often be found that considerable glue or other bodies are eliminated in this manner and that consequently it will be desirable to properly scour the entire lot of silk. The scouring is easily conducted by using a hot soap bath prepared with 2 to 4 ounces of good olive oil soap per gallon and running at a temperature of 160 to 200° F. for one-half to one hour. When unevenness in dyeing or bleaching is observed in the case of spun silk the first observation to be made should be that of the original silk yarn to see if there is any contamination with loading or stiffening agents which are subsequently removed by a scouring operation.

[12] *Jour. Soc. Chem. Ind.*, 1893, p 327.

14. The Scouring of Tussah Silk.

Tussah silk, and wild silk in general, is more difficult to scour than ordinary silk. This is due to the fact that the fiber contains much more mineral matter, and the gum is harsher and more resistant to the action of soap solutions. For general purposes, however, the usual method of scouring ordinary silk is practiced, only the scouring is repeated and prolonged sufficiently to give the desired results. The sericin in the case of tussah silk not only surrounds the fiber externally, but more or less impregnates it. On this account the sericin is not completely removed by boiling soap solutions alone, but the addition of some soda ash, or even caustic soda, is required. On account of the large quantity of brown coloring matter removed from the fiber in the degumming of tussah silk, the boiled-off liquor cannot be used for general purposes of dyeing, as is the case with ordinary silk. The cheapest method of degumming tussah silk is to treat with a solution containing 8 to 10 percent of soda ash at a temperature near the boiling point. This bath is then followed by one containing 10 to 15 percent of soap.

For the scouring or discharging of tussah silk, Beltzer recommends the use of a cocoanut-oil benzene soap (Kokos-Benzoap). This soap contains about 10 percent of benzene, and possesses great emulsifying powers, readily dissolving the gums, resins, oil and sericin present in the silk. The bath is prepared with 10 parts of the soap to 100 parts of soft water at 120° F. When the soap has dissolved, 2 to 5 parts of sodium perborate are dissolved in the solution without raising the temperature. The tussah silk is brought into this bath which is then slowly heated up until a permanent lather is produced. The process requires 3 to 4 hours for the removal of the gum. The bath can be employed twice for scouring and may then be used as a soap bath for dyeing.

Pentecost[13] gives the following results of experiments made on reeled tussah silk to determine the best scouring agent to use in stripping and boiling-off:

(1) Stripped ½ hour and boiled 1 hour in ¼ ounce of soda ash to 1 pint of water;

(2) Treated in a similar manner with a solution containing ⅛ ounce of soda ash and ½ ounce of soap to 1 pint of water;

(3) Treated in a similar manner with a solution containing ⅛ ounce of caustic soda to 1 pint of water;

(4) Steeped for 12 hours in a solution containing 3 pints of water, ½ ounce of soap, 3 c.c. of ammonia water, and 1 c.c. of turpentine.

The samples treated as in (4) looked the cleanest and best, while (3) showed a better color than either (1) or (2), but was not quite as lustrous. On bleaching these four samples, however, with hydrogen peroxide it was found that (4) did not bleach well, the turpentine evidently interfering with the result; (1), (2), and (3) bleached up very much alike in color, though (3) was not quite as lustrous.

Stead recommends the following method for the boiling-off of tussah silk: For 100 pounds of the silk, use a bath containing 250 gallons of water, 5 pounds of potassium carbonate and 20 pounds of a

[13] *Jour. Soc. Chem. Ind.*, 1893, p 330.

good neutral soap, although a slight trace of alkali is not objectionable. The silk is entered at a temperature of 90° F. and given several turns; the temperature is then gradually raised to 200° F. for 30 minutes. The skeins are then lifted and passed into a second bath similar to the first and given a further treatment for 30 minutes, after which a thorough washing with warm water is given in order to remove all traces of soap. The silk is then soured in a solution of hydrochloric acid at 1° Tw. for 15 minutes at a temperature of 85° F., after which a final washing is given to remove all traces of acid.

According to Silbermann, the coarser varieties of tussah silk are first rinsed in a weak solution of soda ash, then treated for one-half

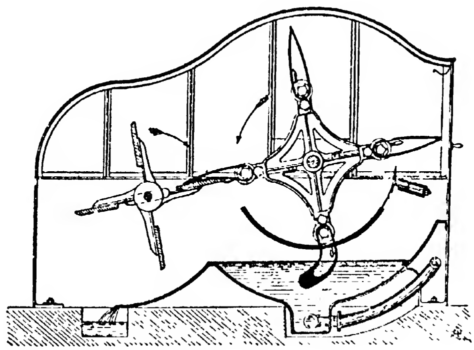

FIG. 91.—Washing and Striking Machine for Silk Skeins.

hour at 105° F., in a bath containing 5 percent of soda ash; the bath is drawn off and the silk is entered into a fresh bath containing 30 percent of soda ash at 105° F. and the temperature is gradually raised to about 200° F. and continued at that temperature for one hour. The silk is then rinsed in fresh water and brightened in a bath containing 10 percent of hydrochloric acid for 10 minutes. Finer qualities of tussah silk are scoured at 140° F. in a bath containing 10 to 15 percent of soda ash and then boiled-off in a bath of 205° F. containing 30 percent of soap, and finally rinsed well and soured as above. It is also said that good results are obtained by degumming in a bath at 140° F. for one-half hour containing 6 to 8 percent of caustic soda.

15. Boiled-off Liquor.

When soap solutions have been used several times for scouring successive lots of silk they become so charged with silk-glue as to be no longer available for scouring purposes. Such a solution is known under the name of "boiled-off liquor," and is preserved for use in the preparation of dye-baths for the dyeing of silk, for which purpose the amount of boiled-off liquor is about one-tenth to one-third the total amount of the dye-bath.

Boiled-off liquor has a light brown color and is rather glary in

appearance on account of the large proportion of soap it contains. It usually has a gravity of 1½ to 2° Tw. It contains about 3 ounces of solid matter per gallon, of which about 2 ounces are soap.

Sometimes boiled-off liquors are not preserved, but are simply run to waste. Disposal in this fashion, however, will cause stream pollution and will also represent a large waste of soap which is possible of recovery. In some mills very efficient by-product recovery plants are operating with the result that most of the soap is recovered in the form of fatty acid.

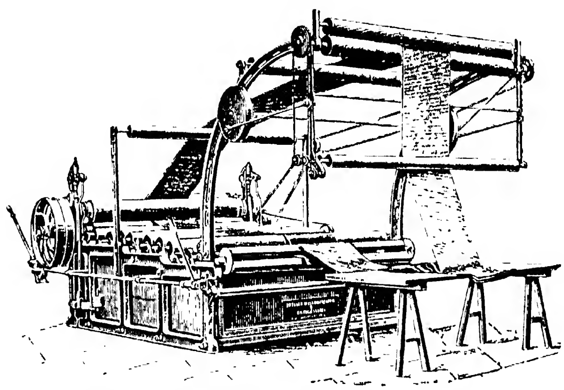

FIG. 92.—Open Width Washer for Silk Pieces

One of the principal methods of recovering by-products from boiled-off liquors is to precipitate the soap by the addition of sufficient lime water. The insoluble lime soap is filtered off and is then decomposed by treatment with hydrochloric acid and boiling so that the free fatty acid is liberated. This floats on the top of the liquor, and is collected, purified, and used again in the manufacture of soap. In this process the alkali and the silk-glue are run to waste. As there does not seem to be any technical use for silk-glue, no attempt as yet has been made to recover it on a commercial scale.

16. Influence of Water in Silk Scouring.

The character of the water employed for the preparation of the soap baths has much to do with success in the boiling-off of silk; if hard water is used, insoluble soaps will be formed which will stick to the silk fiber and which are very difficult to satisfactorily remove. Such water should always be properly softened by treatment with alkalies, so as to remove all of the lime and magnesia compounds, and then filtered.

As silk is such a high-priced material every care should be taken to preserve its valuable qualities to the utmost; on this account only very soft water should be employed in scouring, washing and dyeing this fiber. The usual water obtained from natural sources, as a rule, is not sufficiently soft for use with silk, and consequently a suitable softening

process for the water should always be used. Of late years the method of softening water by the Zeolite treatment, as in the Permutit and Refinite systems, has been largely used by silk mills, as by this method a water of zero hardness can readily be obtained and the quality of the silk can be much enhanced.[14]

17. Apparatus Used in Scouring Silk.

Silk is stripped or degummed mostly in the form of skein yarn, for which purpose specially constructed machines are used so that single skeins of silk are held on rotating porcelain arms in the scouring bath. Woven silk fabrics are very seldom degummed, though half-silk of either silk-cotton or silk-wool is frequently scoured.

The vats employed for the boiling-off of silk are generally rectangular wooden tubs, lined on the inside with canvas to prevent the delicate silk fibers from catching on the roughened surface of the wood. Actual boiling of the solution should be avoided, as this would tend to entangle the silk threads, which, in the case of fine counts of silk, is a serious matter. The hanks of silk are suspended on smooth wooden sticks and thus suspended in the hot soap solution, in which they are left for 1 to 2 hours, being turned by hand from time to time. Sometimes sticks are used which are coated with enamel so as to be smooth and clean; or thick glass rods may be used, though these are very liable to be broken and in consequence are quite costly.

Where all of the silk-glue is removed from the fiber and the pure fibroin alone is left, the individual silk filaments become separated from one another, and unless certain precautions are taken in the handling of the hanks of yarn, the threads become seriously entangled. This is usually prevented by enclosing the hanks of yarn in linen bags, and then boiling in the soap solution until all of the gum has been removed. When the silk skeins are placed in cloth bags or "pockets" these are simply packed into the scouring vat and boiled in the soap-liquors. Under the circumstances much less liquor is required per pound of silk (about 4 gallons per 10 pounds of silk is usually the requisite amount). In case of silk twisted into heavy counts, such as embroidery silk, this method of handling will not be necessary. Machines in which the silk skeins are kept in a stretched condition are also used for the complete scouring of silk to prevent the entanglement of the fibers. The rotary Klauder-Weldon machines are very suitable for this purpose, and are largely used by silk dyers and scourers in this country. By the use of such a machine, the time of handling the material necessitated by tying it up separately in small linen bags is much shortened.

When boiling-off small lots of silk, copper tanks are mostly used. Care should be taken in this case to avoid metallic stains from the verdigris that is likely to form on the copper surface by the combined action of the soap liquor and the air. By keeping the vats clean, however, there is little danger of stains arising on the silk.

The scouring vats should be heated with a closed steam coil, for the use of a perforated steam pipe and the consequent blowing of live steam

[14] See page 47 for descriptions of water softening apparatus.

through the liquid will tangle the fine silk threads; furthermore, the introduction of live steam into the bath will seriously dilute it with the water of condensation, and this is not at all desirable as the baths are nearly always used as standing kettles.

Special forms of apparatus are used where the foam method of boiling-off is employed, as in this case the silk skeins do not come in contact with the liquor at all, but simply with the foam from the liquor.

Chapter X.

Bleaching of Silk.

1. General Considerations.

The silk fiber, being very similar in its chemical properties to wool, is bleached in much the same manner; that is, by the use of sulfurous acid or with sodium peroxide. In the case of yellow-gum silk, where it is desirable to preserve a considerable amount of the gum, the bleaching is frequently preceded by a treatment with nitric acid which has for its purpose the destruction of the yellow coloring matter in the gum. Yellow-gum silk is bleached with *aqua regia* of 3° Bé. before soupling, and is then sulfured. White-gum silk requires sulfuring only, or the yellow tone may be corrected by tinting with Methyl Violet. Yellow-gum silk will bleach up as white as the other silk, for it must be borne in mind that the yellow color of such silk is in the gum and not in the fiber itself. A great deal of the best Italian silk has a yellow gum. When this is removed by proper boiling-off, the silk fiber proper is left in a fine white condition. But when all of the gum is not removed, as in the case of écru or soupled silk, it may become necessary to bleach out the yellow color from the gum as described above.

2. Bleaching Silk by Means of Aqua Regia.

This method is seldom employed for the bleaching of boiled-off white silk, but only as a preliminary treatment to the bleaching of yellow-gum silk where the after-bleaching is to take place with the use of sulfurous acid. The method is carried out in the following manner: The yellow silk is first softened and cleaned by working for about one hour in a warm bath consisting of a ten percent soap solution. It is then well washed to remove all trace of soap and is immersed in a bath of *aqua regia* standing at 3 to 4° Tw. The *aqua regia* is made by mixing five parts of commercial hydrochloric acid with one part of nitric acid, and allowing to stand for 4 to 5 days at 75° F. The silk is steeped in this acid bath until it turns greenish, after which it is taken out, well washed, treated with sulfurous acid and soupled.

When bleaching silk with *aqua regia* or with nitrosyl-sulfuric acid the bath must be made up in a stoneware tank on account of the corrosive nature of the acid. Care must be taken not to steep the silk in the acid liquor for too prolonged a time as it may acquire a permanent yellowish tint from the action of the nitric acid on the fiber.

Instead of using *aqua regia,* a nitrosyl-sulfuric acid may be employed prepared from the chamber crystals occurring in the lead cham-

bers in the manufacture of sulfuric acid. This substance is sometimes called "nitrose" by the dyer. The acid bath is used at a strength of 4° Tw. and the silk is immersed in it for 10 to 15 minutes. If the acid treatment is too long the silk will acquire a yellow tint which cannot subsequently be removed. After steeping in this acid bath, the silk is well washed and sulfured, and soupled as before. The nitrosyl-sulfuric acid solution may also be prepared by using a 10 percent solution of sodium nitrite strongly acidified with sulfuric acid.

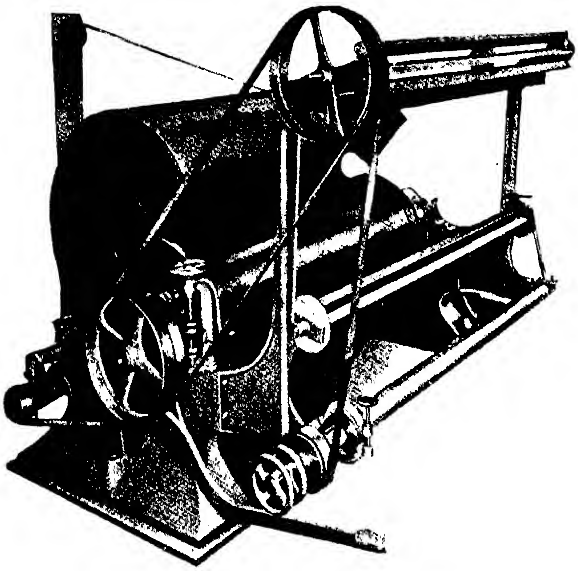

FIG. 93.—Cloth Centrifuge for Silk Pieces.

It has also been suggested to bleach silk with a bath containing 5 percent of sulfuric acid and 1 percent of sodium nitrate. The silk must be thoroughly rinsed immediately after leaving this bath or it will be spotty.

According to Knecht, yellow silk is best bleached by means of nitrous acid (sodium nitrite and hydrochloric acid) but no details of the process are given. In the opinion of the present author this is an erroneous statement as nitrous acid causes a diazotization of silk and has no bleaching effect on the fiber.

3. Bleaching Silk with Sulfurous Acid.

The principle of this method is the reduction of the coloring matter with the sulfurous acid, which may be employed in either the form of sulfur dioxide gas or as a solution of sulfur dioxide or sodium bisulfite

in water. The method of treatment is very simple; the silk, after boiling-off or soupling, is hung up in a suitable chamber where it may be exposed for 4 to 6 hours to the action of the fumes of burning sulfur, in case of the gas bleach, or steeped in a solution of sodium bisulfite, in case of the liquid bleach. About ½ pound of sulfur is required to be burned per 1000 cubic feet of space in the bleaching chamber when the gas method is employed. This will usually result in the use of 5 pounds of sulfur for 100 pounds of silk.

As with wool, the sulfurous acid bleach on silk is not a permanent one, for the yellow color returns after some time. This is probably due to the re-oxidation of the reduced coloring matter with the result

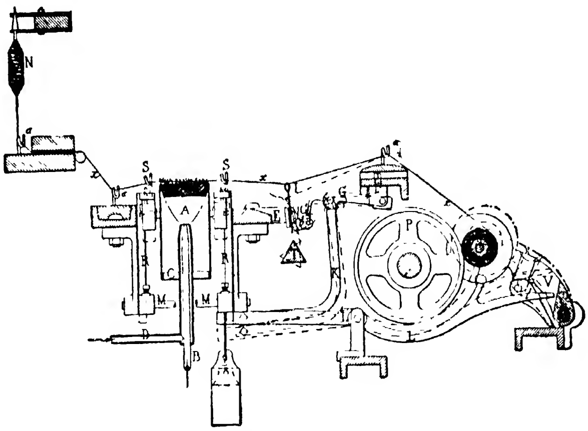

FIG. 94—Gas Singeing Machine for Silk Yarns.

that the original pigment is formed again. The sulfur bleach on silk is also destroyed to a greater or less extent by an after-treatment with soap or alkaline baths, so that this method of bleaching is of little use for silk which is to be dyed subsequently in light colors where a soap is used. On account of its cheapness, however, the sulfur bleach is still largely employed for silk. The use of sulfur dioxide gas, in the case of silk, is much more efficient as a bleaching agent than solutions of sulfurous acid or of sodium bisulfite, on which account the latter are very seldom employed in connection with silk, though considerably used for the bleaching of wool.

4. Use of Sodium Hydrosulfite.

Sodium hydrosulfite may be used for the bleaching of silk. The solution is prepared in the manner already described in previous pages under the bleaching of wool. The soupled silk is steeped in the solution for six hours, and then well wrung out and immediately washed. If the washing is delayed too long the silk will heat up and become injured in luster and strength. After washing, the silk should be run through

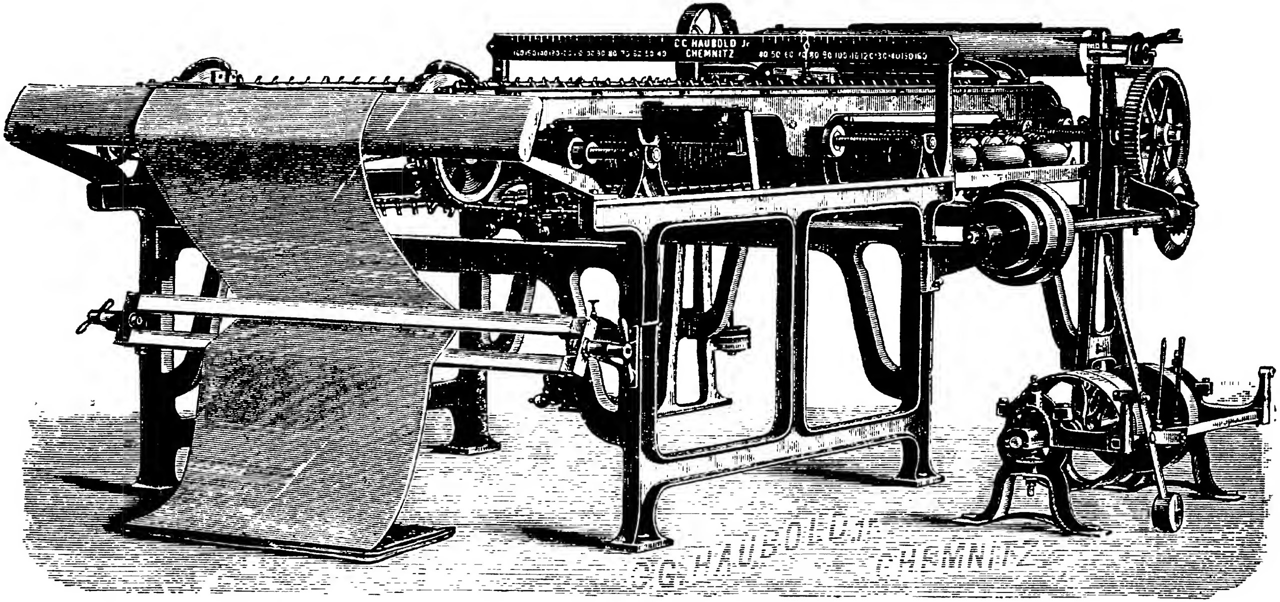

Fig. 95.—Steaming Machine for Silk Pieces.

a bath of dilute hydrochloric acid in order to remove all traces of zinc compounds, otherwise yellow stains are liable to develop. After the acid bath the silk is finally well washed in water.

5. Bleaching Silk with Peroxides.

Hydrogen peroxide has been used for a number of years for the bleaching of silk, but it is now giving place to the cheaper sodium peroxide. The principle of the bleaching action depends on the oxidation of the coloring matter by means of the solution of hydrogen peroxide employed. Whether hydrogen peroxide itself is originally employed or solutions of sodium peroxide makes no difference in the essential action from a chemical point of view, for the solution of sodium peroxide also gives hydrogen peroxide, so the same agent acts in either case. The bleach obtained in this manner is one of oxidation, and leads to the ultimate destruction of the coloring matter, so that

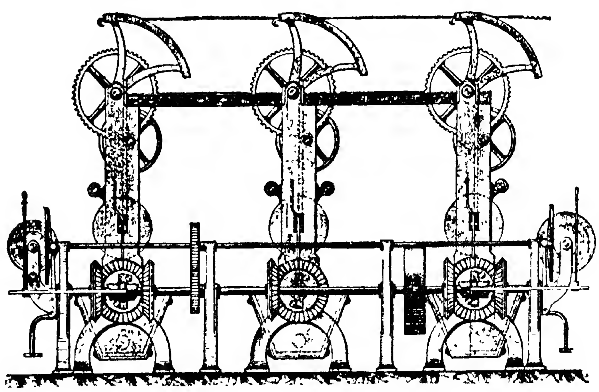

FIG. 96.—Crabbing Machine for Silk Pieces.

this bleach is a permanent one, and therein is better than the sulfur bleach.

Solutions of hydrogen peroxide may be employed either cold or hot for the bleaching of silk. In the former case, the bath is prepared by diluting a quantity of 12-volume solution of hydrogen peroxide with three times its volume of cold water, and adding sufficient ammonia to cause the liquid to smell of it distinctly. The bleaching bath may be prepared as follows: for 100 pounds of silk use a bath containing 130 gallons of water, 25 gallons of hydrogen peroxide, 12 pounds of sodium silicate and 12 pounds of soap dissolved in water. Immerse the silk completely and use the bath at 130° F. After the silk is bleached sour with weak sulfuric acid and then rinse thoroughly to remove all the acid. Instead of ammonia, borax, magnesia, and silicate of soda may be used as the alkali. The silk is immersed in this bath for 12 to 48 hours, according to the desired extent of the bleaching. It is not wise to leave the goods in longer than three days, as otherwise the luster and

strength will be impaired. When employed hot the hydrogen peroxide bath is made up with 1 part of 12-volume hydrogen peroxide and from 10 to 20 parts of water, according to the degree of bleaching desired.

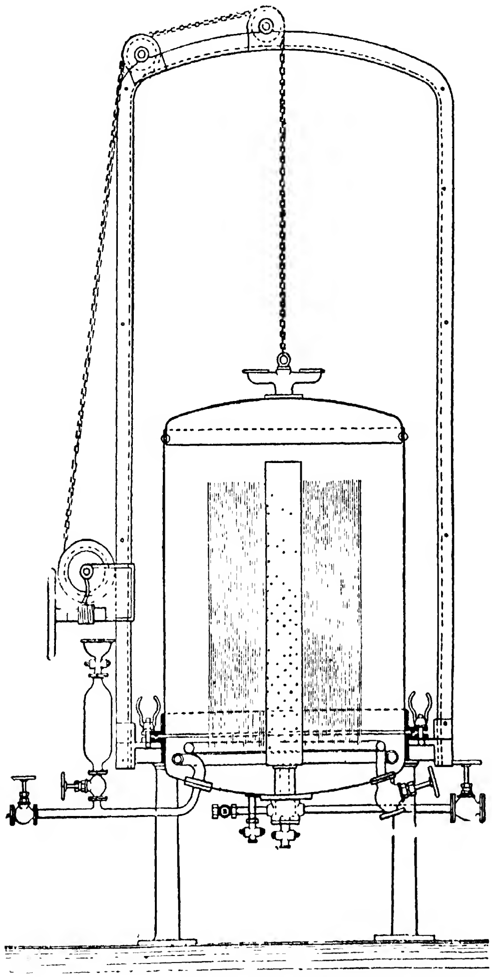

FIG. 97.—Steaming Apparatus for Silk-wool Pieces.

Either ammonia or the other alkalies mentioned above are added, and the silk is entered and worked for 15 minutes, after which the bath is gradually heated up to 190° F. during one hour, and then maintained

at that temperature for 45 minutes, after which the silk is washed off.

Owing to the expense of hydrogen peroxide, this has now been largely replaced by sodium peroxide. The peroxide bath for silk may be prepared as follows: for 100 pounds of silk use a bath containing 160 gallons of water, stir in 10 pounds of concentrated sulfuric acid, and then cautiously add 7½ pounds of sodium peroxide; then add 5 pounds of sodium silicate and finally a solution of 5 to 10 pounds of soap. Use the bath at 180° F. The bath of sodium peroxide is made up in the manner already indicated under the bleaching of wool (see page 138), and the details of the bleaching operation are carried out in the same manner. Great care must be had in the preparation of the sodium peroxide bath and also that all the chemicals and vats employed are free from traces of iron, otherwise the bleach obtained will not be satisfactory.

6. Bleaching Silk with Potassium Permanganate.

Silk may be bleached with this reagent in much the same manner as wool (see page 145). The silk is first soaked for 15 minutes in a cold bath containing 1 pound of potassium permanganate to 10 gallons of water. It is then squeezed and treated in a bath containing sulfurous acid (or sodium bisulfite and sulfuric acid) until the brown color which it first acquires is changed to a white. Care should be taken that the action of the chemicals should not be too prolonged and the baths should be used cold.

7. Bleaching Silk with Perborates.

Like sodium peroxide the perborates (sodium or magnesium) are capable of forming hydrogen peroxide in solution under proper treatment. On this account sodium perborate in particular has been recently put forward as an available bleaching agent for wool (see page 147) and silk.

Sodium perborate is prepared from sodium peroxide and boric acid, and as compounds derived from borax are all rather expensive when compared commercially with sodium compounds alone it is reasonable to expect that sodium perborate would be more costly than sodium peroxide when based on an equivalence of available oxygen. Furthermore, commercial sodium perborate contains only 10.4 percent of active oxygen, whereas sodium peroxide contains about 20 percent or practically twice as much.

In its general application to purposes of bleaching, sodium perborate is very similar to sodium peroxide or hydrogen peroxide. In fact, the various per-oxygen chemical compounds which have from time to time been suggested as capable bleaching agents, such as perborates, percarbonates and persulfates, all depend in the last resort for their bleaching activity on the fact that they readily furnish a solution of hydrogen peroxide when dissolved in water or when their solutions are treated with a suitable acid. Therefore, the bleaching process with all these reagents comes down to a question of bleaching with hydrogen peroxide. In the consideration of this question, the chief

factors to be reckoned with are the comparative amounts of hydrogen peroxide formed from equal quantities of the different compounds and the relative cost of hydrogen peroxide thus produced and whether the decomposition of the product brings into the solution other ingredients

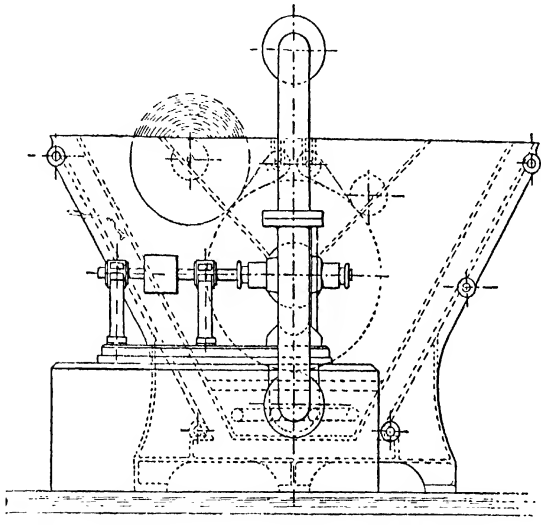

FIG. 98.—Special Machine for Degumming Silk Pieces.

which may hinder the activity of the hydrogen peroxide in its bleaching efficiency. Sodium perborate is much more stable in its nature than sodium peroxide and it was principally on this account that it attracted

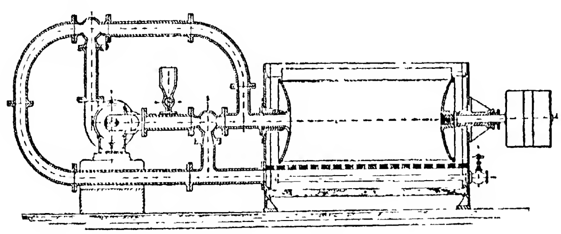

FIG. 99.—Cross-section of Degumming Machine.

attention for purposes of bleaching. Whereas sodium peroxide would decompose with violent rapidity when dissolved in cold water, sodium perborate requires to be dissolved in hot water in order that it may be decomposed completely and the resulting products are hydrogen peroxide and borax. It may be probable, however, that some or all of the

borax exists in the solution as metaborate of sodium. It has not been demonstrated that bleaching baths prepared from sodium perborate are as efficient as the bath containing pure hydrogen peroxide alone, and solutions prepared from sodium perborate show a relatively higher cost for the same amount of active bleaching agent. In this respect, sodium perborate is expensive out of all proportion when compared with sodium peroxide. The liberation of hydrogen peroxide in perborate solutions may also be brought about by the addition of an acid, in which case an organic acid, and preferably formic acid, should be

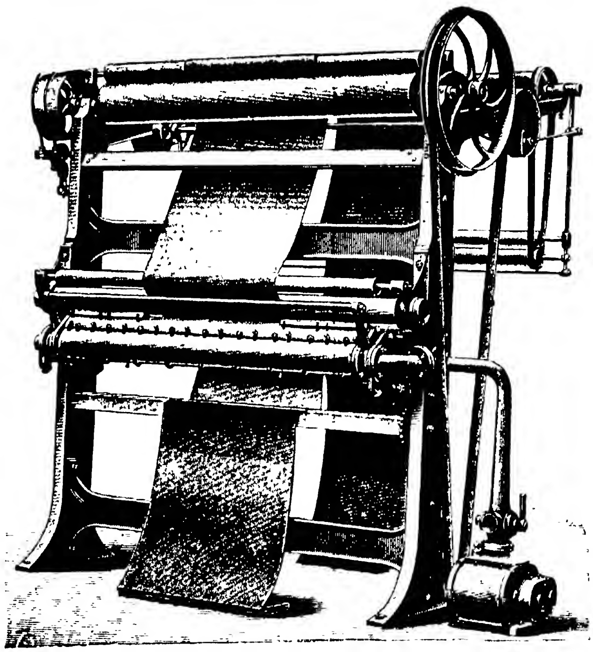

FIG. 100—Singeing Machine for Silk-cotton Goods.

used. There are a number of perborates possible, ranging in active oxygen content from about 4 percent to 16 percent. The best commercial samples, however, of sodium perborate show about 10 percent of active oxygen.

According to a German patent, yarn or fabrics may be padded with a cold solution of sodium perborate and then steamed and washed and the process repeated until a sufficient degree of bleaching is procured. Lime may be added to the perborate solution. The amount of perborate used is said to be much less than in the usual process, being only that taken up by the material, and it is further claimed that this process gives more rapid results.

Perborates are usually recognized by producing an intense blood-red color with titanic acid in the presence of sulfuric acid. Also solutions of sodium bichromate are turned blue on the addition of perborates, and this test can be used to indicate when the exhaustion of the perborate bath is completed.

Percarbonate of soda has also been suggested for the purpose of bleaching expensive silk materials. This compound is prepared electrolytically by passing a current of electricity through a concentrated solution of sodium carbonate at a low temperature. The solution of the electrolyte must be rather concentrated in order to allow the less soluble percarbonates to separate out. By dissolving sodium percarbonate in hot water, there is formed a solution of hydrogen perborate and sodium carbonate. Therefore, in the bleaching of silk with this material, it is advisable to use an acid bath, it being recommended to dissolve the sodium percarbonate in cold water and then to acidify with formic acid.

The only persulfate which has been suggested for bleaching purposes is the ammonium salt. It is far too expensive, however, for use on a commercial scale, although it has considerable value in certain bleaching processes on an experimental scale. Ammonium persulfate is made by the electrolysis of ammonium sulfate. It is a solid and is used for bleaching by dissolving in cold water. The bleaching bath is used warm and its action is usually powerful. A by-product formed in this solution is ammonium acid sulfate.

8. Bleaching Tussah Silk.

Tussah silk is much more difficult to bleach than mulberry silk, on account of the greater amount of impurities in the fiber, and also by reason of the fact that the fiber is less amenable to the action of chemical reagents. As already mentioned under the subject of silk scouring (see page 169), tussah silk is much more difficult to strip than mulberry silk; that is, the sericin is hard to remove, and as the stripping must precede the bleaching of silk, it can readily be understood that the bleaching of tussah silk is not a simple problem. Probably the best method for bleaching tussah silk is in the use of sodium peroxide, for the sulfuring method does not seem to give satisfactory results.

After degumming tussah silk the fiber still possesses a rather dark brown color; in this respect it differs from mulberry silk, as the coloring matter is not present in the layer of gum, but also permeates the entire fiber. On this account the bleaching of tussah silk is by no means easy as it requires vigorous action to destroy the brown pigment matter. At the present time, the peroxide method is chiefly used for bleaching tussah silk, the strength of the bath, the temperature and the duration of treatment depending on the quality and natural color of the silks and on the degree of whiteness desired in the bleach.

According to Haen, the following process is recommended: For 50 pounds of tussah silk a bath is prepared containing 30 pounds of magnesium sulfate dissolved in 110 gallons of water. The silk after being well boiled-off and washed, is thoroughly impregnated with this liquor,

and then lifted from the bath, while 6 pounds, 10 ounces of sodium peroxide is carefully added in three portions during 45 minutes, working the silk in the bath after each addition. It is important not to neglect to first impregnate the silk with the magnesium sulfate solution, otherwise the luster of the fiber would be impaired by the strongly alkaline solution of sodium peroxide acting on the silk. After the final addition of the sodium peroxide, the bath is heated during 45 minutes to 190° F. Dilute sulfuric acid is then added to clear the liquor which will have become milky through the precipitation of magnesium hydrate. The silk is then given two to three turns in this liquor, washed and worked for 30 minutes in a bath containing 30 percent of soap for the purpose of restoring and increasing the luster; it is finally washed and brightened. Zinc sulfate may be employed in place of the magnesium salt, but does not give as good results.

There have been a number of other methods proposed for the bleaching of tussah silk, but apparently without any practical basis. Lunge has described a method combining the sulfuring process with the sodium peroxide method.[1] The silk is first sulfured or bleached with sodium bisulfite and is then steeped in a bath made of 7 gallons of water, 1½ gallons of hydrogen peroxide and 1½ pounds of sodium silicate for several hours. As these two processes are diametrically opposed to each other in principle, the one being a reduction while the other is an oxidation, it might be expected that they would mutually neutralize each other more or less; and experience proves this to be the case, for sulfuring and then bleaching with sodium peroxide does not give any better results than by using the sodium peroxide solution alone. Koechlin's method (given by Hurst) was to use hydrogen peroxide in connection with caustic soda, soap and magnesia at a boiling temperature. Koechlin's method is given as follows: prepare a bath with 22 gallons of water, 22 pounds of caustic soda, 66 pounds of soap, 11 pounds of calcined magnesia, 11 gallons of hydrogen peroxide and a little ammonia; the silk is boiled in this liquor for several hours. Girard's method, which has been used to some extent in Europe, is as follows: (*a*) the tussah silk is worked in a warm dilute (1 to 8) bath of hydrochloric acid for one hour; (*b*) wash and boil-off with a 5 percent solution of sodium carbonate or a 2 percent solution of caustic soda and wash again; (*c*) steep in a weak solution of ammonium hypochlorite for 24 hours (this solution is prepared by mixing together solutions of bleaching powder and ammonium carbonate, allowing to settle and using the clear liquor); (*d*) wash and pass into a dilute bath of hydrochloric acid at 2° Tw. and wash again; (*e*) steep for 24 hours in a bath of hydrogen peroxide of ½ volume strength with the addition of ammonia or borax. The function of the first treatment with hydrochloric acid is to remove the lime present in tussah silk. The treatment with ammonium hypochlorite is considered by Pentecost as being superfluous, as no advantage is gained over the bleaching with hydrogen peroxide alone. From experiments made by the latter-named writer[2]

[1] Hurst, *Silk Dyeing*, p. 32.
[2] *Jour. Soc. Chem. Ind.*, 1893, p. 331.

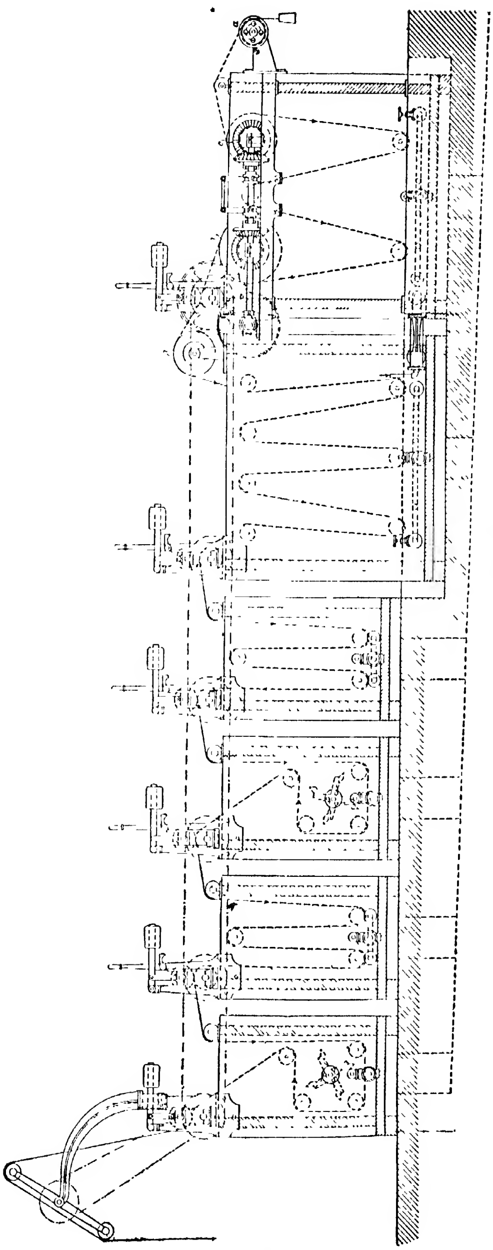

Fig. 101.—Boiling-out Machine for Silk-cotton Goods.

it appears that the best conditions for bleaching tussah silk with hydrogen peroxide is to use 1 part of 12 volume hydrogen peroxide with 10 parts of water, adding to the bath ¼ ounce of sodium silicate for each 22 ounces of the bath; the silk is steeped in such a solution for 2 days cold, and then heated to 190° F. for 2 hours. Ammonia, magnesia and borax do not give as good results as sodium silicate as additions to the bath.

Beltzer recommends the use of hydrogen peroxide and hydrosulfite compounds, the bleaching being effected in two stages. Hydrogen peroxide solution of 6 to 10 volumes strength is made faintly alkaline

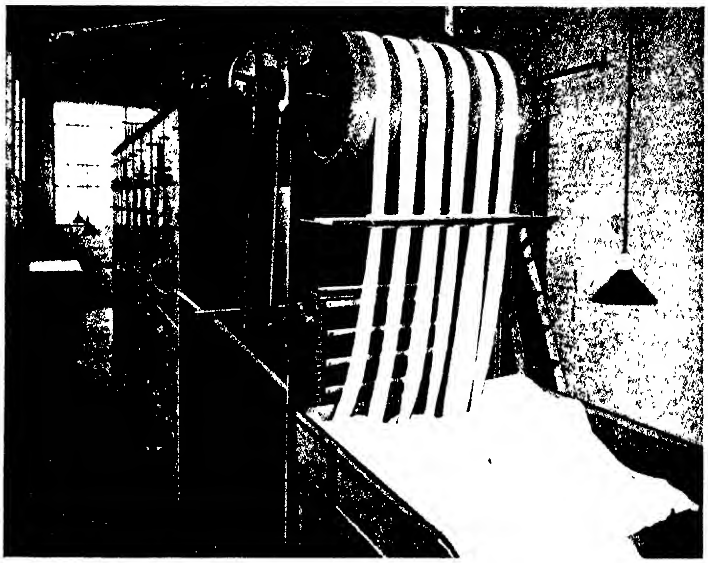

Fig. 102.—Drying Machine for Silk Crêpe (Proctor & Schwartz).

with ammonia, then heated to 100° F. The silk is completely immersed in this solution, where it is allowed to remain for 24 hours. In practice it is customary to give the silk a preliminary treatment in a peroxide bath which has already been used once. The bleached silk is washed in soft lukewarm water, and is then soured in a solution containing 1 part of oxalic acid to 1000 parts of water for 3 to 4 hours at a temperature of 160° F. After passing through this treatment the silk is of a pale yellow color. To give the final bleach a solution is made with 1 part of Blankit (or other similar hydrosulfite compound) to 100 parts of water at 120° F. The well washed silk is immersed in this solution for 24 hours, then rinsed in soft water and dried at a low temperature. It should then have a fine lustrous white appearance. The hydrosulfite

may be used repeatedly, being freshened up each time with the necessary amount of Blankit. The strength of the bath may be determined by titration with indigo-carmine solution.

From a study of the different processes of bleaching tussah silk, Stead recommends the following method: For 100 pounds of silk a bath is prepared containing 250 gallons of water to which is added 26.6 pounds of sulfuric acid (168° Tw.) and 20 pounds of sodium peroxide, the excess of acid being then neutralized by the addition of a slight excess of sodium silicate. The previously boiled-off silk is entered into this bath and in the course of 30 minutes the temperature is gradually raised to 140° F. The silk is turned occasionally during 6-8 hours, when the bleach should be complete. The silk is then removed and thoroughly rinsed in tepid water, and next passed into a warm dilute solution of sodium bisulfite to which is added a small quantity of hydrochloric acid. After an immersion of 15 minutes in this bath the silk is removed and well washed to remove all traces of acid, and finished according to requirements.[3]

9. After-treatment of Bleached Silk.

After silk yarn has been scoured and bleached, it may be either used for subsequent dyeing or it may be employed directly as bleached material for the purpose of weaving or other processes of manufacture. In the latter case, after the silk has been bleached, it is usually weighted with stannic chloride, but as this is a process employed as an adjunct in dyeing, it will not be considered at this point. There are various mechanical treatments, however, which are customarily given to the bleached silk in the skein form, and these include scrooping, shaking-out, stringing, and lustering.

(*a*) *Scrooping.*—This is for the purpose of giving the silk fiber a stiff or harsh quality so that when squeezed or rubbed, it emits a crackling or crunching sound. Contrary to the popular opinion, this property of scroop is not one that is natural to the silk fiber itself but is an acquired property given to it by special treatment. For the scrooping of silk, the material is usually steeped in a bath of tartaric acid (containing about 5 grams per liter) until the fiber is thoroughly impregnated with the solution, then squeezed out and dried without rinsing. Another method which is recommended is to first pass the silk through a weak soap bath, squeeze out, and then steep in the tartaric acid bath as before, and finally squeezing and drying without rinsing. In order to produce a good scroop the silk must not be oiled as this will prevent the development of the characteristic "crunch."

(*b*) *Shaking-out.*—This process is termed by the French *sécouage* and is used to open out the skeins of silk so as to straighten the threads and separate them from each other. It also gives the silk a uniform appearance and lessens the tendency of the fiber to curl and wrinkle. This process is usually performed after drying and simply consists of hanging the skeins of silk on a wooden peg or support and by means of a smooth stick, pulling and shaking out the skeins in a vigorous manner. Special machines are also built for carrying out this operation, thus saving hand labor and giving more uniform results.

(*c*) *Stringing.*—This is termed by the French *chevillage* and was formerly a process used in conjunction with the shaking-out operation. Its purpose is to straighten-out the threads and to separate the double silk fibers into individual filaments and also to add luster or gloss to the thread. The operation may be

[3] For the description of various superannuated methods of bleaching tussah silk, see Silbermann, *Färber-Zeit.*, 1893, p. 216.

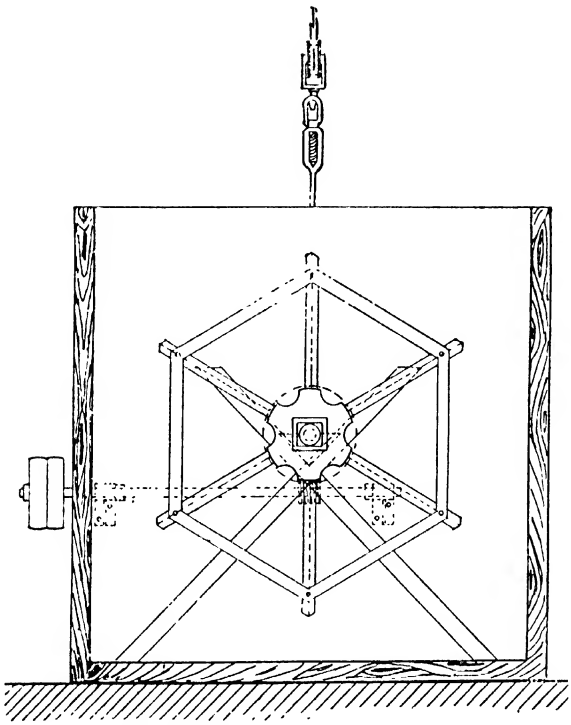

FIG. 103.—Machine for Boiling-off Plush Fabrics.

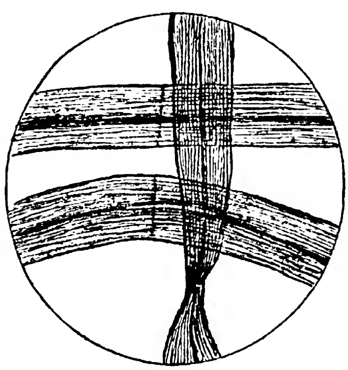

FIG. 104.—Micrograph of Tussah Silk Fibers.

conducted by hand, in which case the dried skeins are hung on pegs and then by means of a smooth stick, the skeins are pulled, and twisted tightly first in one direction and then in another. The operation is now usually conducted by means of a special machine designed for this purpose, the skeins being hung on spindles and automatically twisted first in one direction and then in the other. In some cases the stringing is done simply by twisting the skeins as tightly as possible and leaving them in this position for several hours and repeating the operation over a period of several days. This method is used principally on sewing silks and is for the purpose of giving an increased luster to the fiber.

(*d*) *Lustering.*—This operation is used in conjunction with the preceding and is a final process given to almost all skein silks, whether bleached or dyed. It is for the purpose of giving a high degree of luster to the fiber and also it helps considerably in the subsequent winding of the silk from the skeins. In carrying out the process, a silk lustering machine is used, the silk skeins being stretched between polished steel revolving rollers. These are enclosed in an iron box and while the rollers are turning, steam at a moderate pressure is admitted into the box so that the hot, dry steam acts on the stretched fiber. This process gives the silk a brilliant mother-of-pearl luster.

10. Bleaching of Half-Silk Fabrics.

Half-silk fabrics consist of a mixture of cotton and silk fibers, usually a cotton warp and a silk filling. Ribbons, dressgoods and fancy fabrics are often of this structure. The bleaching of such goods presents certain difficulties, as the ordinary methods of bleaching cotton cannot be applied, as these would ruin the silk fiber, and the usual methods of bleaching silk will not always give a suitable bleach to the cotton. Half-silk fabrics, for instance, cannot be successfully bleached by treatment with hypochlorites, as these have an injurious effect on the silk; while on the other hand sulfurous does not furnish a satisfactory bleach to the cotton, and moreover is liable to tender this fiber by the formation of sulfuric acid.

The only satisfactory method of bleaching half-silk fabrics, therefore, is by the use of peroxides. The goods should first be well boiled-out in a neutral soap solution, taking care to employ a soap free from caustic alkali, as otherwise the silk fiber will be injured and suffer a loss of luster. The bleaching solution is prepared from peroxide of hydrogen or of sodium and should be a rather concentrated one, for if a weak peroxide bath is employed the bleaching action will be too slow, and as a result the cotton will not come up to a satisfactory white while the silk will be liable to turn to a yellowish or brownish color. The vat employed for the bleaching bath should be lined on the inside with canvas, and care should be taken to prevent any metal from getting into the bath. Even lead pipes for heating should be avoided, the steam being introduced by means of a rubber hose. The undesirability of the use of lead pipes is due to the fact that in the strong peroxide bath the liberated oxygen will combine with the lead to form brown lead peroxide which will be absorbed by the silk and will give it a yellowish shade. It is well to use a 3 to 4 percent peroxide bath neutralized with sulfuric acid and heated to 140° F. Just before the introduction of the goods the bath should be made slightly alkaline by the addition of sufficient sodium silicate. As soon as the material has come up to a good white (3 to 6 hours) they should be removed from the bath and rinsed several times, first in dilute oxalic acid, then in water,

Chapter XI.

The Boiling-out of Cotton.

1. General Considerations.

For the general purposes of manufacture cotton does not require to be scoured. The impurities in this fiber may be regarded as those substances other than cellulose which may be present, and mostly include waxy and resinous matters. Far from being a hindrance to the proper processing of cotton during its manufacture these impurities are a considerable aid as they render the fiber plastic and resilient during the carding and spinning operations. It is only previous to dyeing and bleaching processes that it becomes necessary to scour cotton, for the waxy impurities with which the fiber is associated prevent the ready absorption of solutions by the cotton, so that the latter in its raw state is quite water-repellent. This property may easily be shown by dropping some raw cotton on the surface of water; it will be observed that the fibers do not become wetted but float about on the water.

Cotton may be bleached in either one of its three forms (loose stock, yarn, or cloth). Loose cotton is only bleached to a small extent, principally for the preparation of absorbent cotton from cotton comber waste and for the preparation of cotton batting from cotton linters; but for ordinary textile purposes for the preparation of yarns, loose cotton is not customarily bleached. There are, however, certain cases where bleached cotton stock is spun into yarns for hosiery and underwear; for this purpose only a cream bleach is produced. Cotton yarn is bleached in cases where it is to be subsequently dyed in delicate tints and a pure clear color is desired; or when white yarn is to be used in woven cloth together with colored yarns, and it is not advisable to bleach the woven fabric on account of the danger of destroying the colors. Cotton cloth, or calico, is bleached for the purpose of leaving it in the white condition, in which case it is called the "market bleach"; or for dyeing of delicate shades and certain colors, such as Turkey-red, in the piece; or finally, for the purpose of being used as print cloth in the making of calico prints. The bleaching of cotton cloth is a much more thorough and complicated process than the bleaching of loose stock or yarn as it is required, especially when the cloth is to be used for dyeing Turkey-red or for printing, that absolutely all impurities be removed from the fiber.

conducted by hand, in which case the dried skeins are hung on pegs and then by means of a smooth stick, the skeins are pulled, and twisted tightly first in one direction and then in another. The operation is now usually conducted by means of a special machine designed for this purpose, the skeins being hung on spindles and automatically twisted first in one direction and then in the other. In some cases the stringing is done simply by twisting the skeins as tightly as possible and leaving them in this position for several hours and repeating the operation over a period of several days. This method is used principally on sewing silks and is for the purpose of giving an increased luster to the fiber.

(*d*) *Lustering.*—This operation is used in conjunction with the preceding and is a final process given to almost all skein silks, whether bleached or dyed. It is for the purpose of giving a high degree of luster to the fiber and also it helps considerably in the subsequent winding of the silk from the skeins. In carrying out the process, a silk lustering machine is used, the silk skeins being stretched between polished steel revolving rollers. These are enclosed in an iron box and while the rollers are turning, steam at a moderate pressure is admitted into the box so that the hot, dry steam acts on the stretched fiber. This process gives the silk a brilliant mother-of-pearl luster.

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is added in cases where the goods are to be left in the white condition; the object of this being to remove the dead-white appearance of the bleached cotton and to give it a bluish cast which is more pleasing to the eye. The tinting is nearly always carried out simultaneously with the soaping.

3. Nature of Impurities in Cotton.

In the raw state, cotton consists essentially of cellulose associated with 4 to 5 percent of other matters made up principally of pectin,

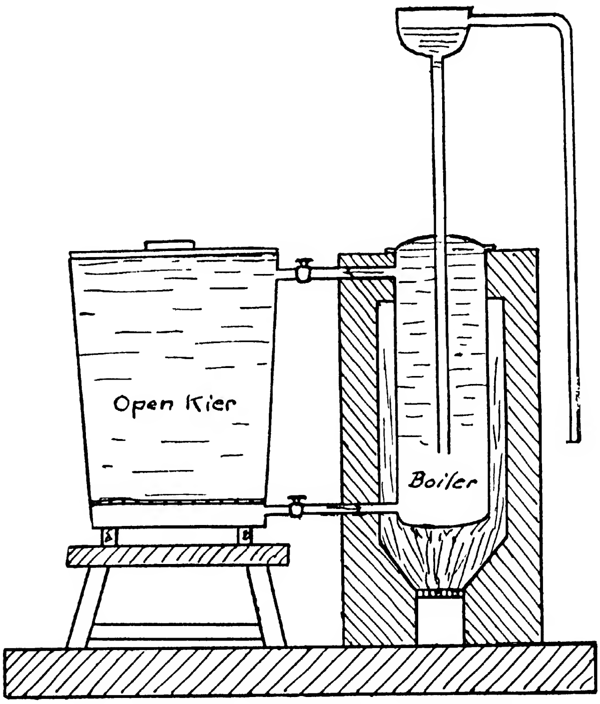

FIG. 106.—Floyd's Apparatus for Boiling, 1795.

cotton-wax, cotton-oil, albuminous matter, coloring matter and a small amount of mineral matter.

The chemical analysis of the raw cotton fiber gives the following results:[a]

	Percent
Water	6.74
Ash	1.65
Protein	1.50
Fiber (cellulose)	83.71
Nitrogen free extract	5.79
Fat	0.61

[a] Bulletin No. 33, of the U. S. Dept. of Agriculture.

The chemical composition of different varieties of cotton from various sources may be said to be practically the same, as variations in the reported analyses are no greater than the variations to be observed in the analyses of different samples of the same kind of cotton.

According to Trotman and Thorp[3] the following analysis represents the composition of the non-cellulose part of the bulk of cotton yarns and fabrics as they are delivered to the bleacher:

	Percent
Water	8-10
Oil, wax and fat	1-5
Mineral matter	1-2
Nitrogenous and other bodies soluble in alkali	4-8

Lester[4] has studied the substances present in raw cotton capable of extraction by water. This extract is evidently of a complex nature and

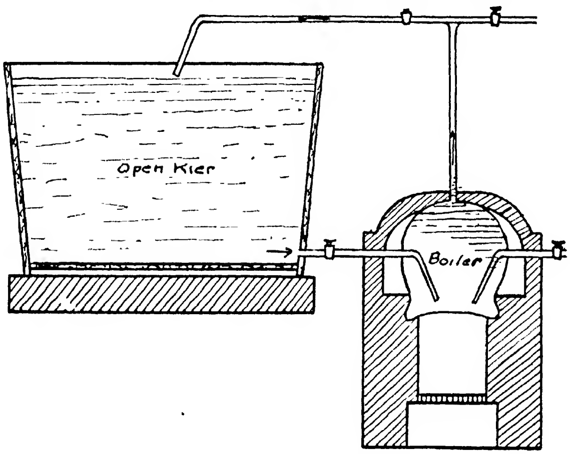

FIG. 107.—Persoz Apparatus, 1846.

amounts to about 1.73 percent from yarn, though if the cotton yarn is clipped up into short lengths of one-quarter inch, the extractive matter rises to 2.11 percent. The analysis of this extract is given as follows:

	Percent
Ash	39.22
Fatty acids	62.30
Ether extract	17.52
Cold water extract	39.50
Ash of original cotton	0.82
Ash of cotton after extraction with water	0.21

Lester also shows that while cotton on exposure to air after drying will reabsorb about 8 percent of moisture, the dried aqueous extract from cotton will absorb about 32 percent and hence is of a far different

[3] *Principles of Bleaching and Finishing Cotton*, page 4.
[4] *Jour. Soc. Chem. Ind.*, 1902, p. 388.

nature from that of cotton. Probably raw cotton owes some of its hygroscopic moisture to this substance.

Knecht[5] gives the following results from an investigation on the extractive matters in raw cotton:

Extracted successively with:	Egyptian, percent	Texas, percent	Bengal, percent
Benzene	0.47	0.55	0.38
Alcohol	0.68	0.90	....
Water	1.46	1.61	....
Ammonia (25 c.c. per liter)	0.48	0.39	....
Formic acid (25 c.c. per liter)	0.46	0 72	....

The extractions were carried out by boiling with the solvents in a Soxhlet tube. The results, however, are so variable that they possess only a comparative significance in giving some general idea as to the amount and character of the extractive matters of the raw fiber.

4. Chemical Analysis of Cotton.

The complete chemical analysis of cotton may be conducted as follows: (1) The hygroscopic moisture may be determined by drying to constant weight at 220° F. or perhaps more accurately by the toluene

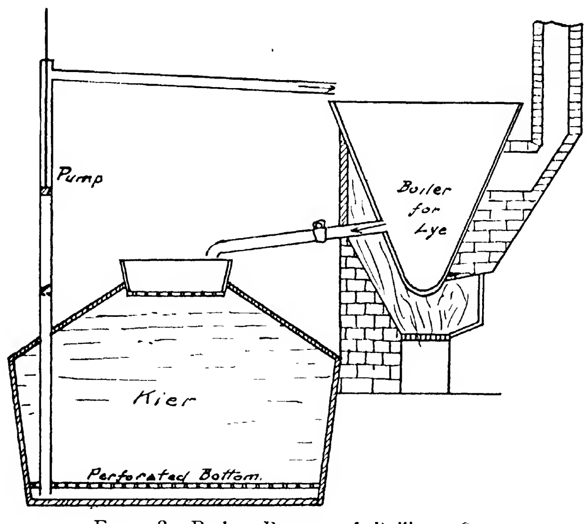

FIG. 108.—Parkes Process of Boiling, 1815.

method of Schwalbe. The toluene method is as follows: 3 grams of the cotton is boiled with 300 c.c. of pure toluene (b. p. 230° F.). The water is collected by distillation in a graduated tube, and from a determination of its volume, or by weighing, the percentage of moisture may be calculated. (2) A weighed portion of the cotton is incinerated

[5] *Text. Inst. Jour.*, 1911, p. 22.

in a platinum or porcelain crucible to a complete ash; this will give the ash of the raw fiber, and it may be subsequently analyzed by the customary chemical methods to ascertain its composition. (3) Another portion of the fiber is boiled with caustic soda solution of 2° Tw. rinsed, and dried; the loss in weight is considered as fat and wax. Or the fibers may be extracted with alcohol and ether in a Soxhlet apparatus, and the extracted matter determined by loss in weight, or ascertained directly by evaporation of the solvent. (4) The amount of nitrogen in the cotton may be determined by Kjeldahl's method. (5) The amount of cuticle is obtained by determining the loss in weight after boiling with a solution of sodium sulfite. (6) The ash of the remaining cellulose can then be determined by ignition. (7) The loss in weight on ignition is cellulose.

A résumé of the complete analysis of cotton is as follows:

(a) Dry at 220° F; loss = hygroscopic moisture.
(b) Ignite; residue = ash of raw fiber.
(c) Boil with caustic soda; loss = fat and wax.
(d) Bleach with sodium hypochlorite solution of 2° Tw.; loss = coloring matters.
(e) Boil with alkaline solution of sodium sulfite; loss = cuticular substance.
(f) Ignite; loss = cellulose.
(g) Residue of ignition = ash of cellulose.

Such an analysis will furnish about the following results:

		Percent
(a)	Hygroscopic water	7.00
(b)	Ash of raw fiber	1.12
(c)	Fats and wax	5.00
(d)	Loss on bleaching	0.50
(e)	Cuticular matters	0.75
(f)	Pure cellulose	86.63
(g)	Ash of cellulose	0.12

5. Pectin Compounds.

Pectin compounds form the greater portion of the impurities present in cotton. These compounds are of a rather indefinite character but consist of gum-like bodies derived from the cell-juices of the plant, and appear to form an integral part of most vegetable cell membranes. Pectin is presumed to be a derivative of pectic acid with metallic salts, and calcium pectate is one of the chief ingredients in the gums which cement together the cells of woody tissues.

According to Bowman [6] in the earlier stages of the growth of the cotton fiber the cell-contents are similar to those contained in the juices of all unripe fruit, comprising a mixture of organic bodies to which the general name of pectose is given. Pectose itself is quite insoluble in water, but during the changes which occur, under the action of sunlight and air and in association with the vegetable acids, it is converted into a definite body known as pectin, which readily dissolves in water and gives a viscous solution. As the ripening proceeds a further change

[6] *Structure of the Cotton Fiber*, p. 246.

occurs, and the pectin is transformed into pectic acid and pectosic acid, which are soluble in boiling water and give solutions which furnish viscous jelly-like bodies on cooling.

Pectin compounds are really the products in vegetable juices that give these the property of forming jellies; pectin is also the chief com-

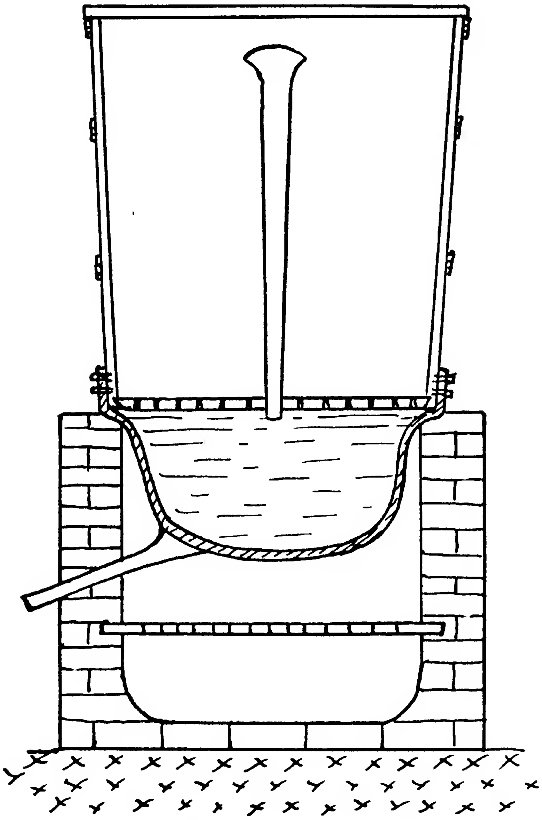

FIG. 109.—Boiling Apparatus of Kurrer, 1831.

ponent of Irish moss and similar vegetable matters. When boiled with alkalies pectin is decomposed, giving sodium pectate together with salts of the organic acids contained in the original pectin. On acidifying the alkaline solution of pectin a precipitate of pectic acid is produced. Calcium pectate is one of the most important salts of pectic acid occurring in vegetable cells and assists considerably in binding together these cells in the composite tissues.

6. Cotton-Wax.

This wax appears to coat the fiber with a protective layer, making it water-repellent. The wax appears to be closely analogous to carnauba wax.[7] It is not soluble in alkalies, but it is gradually emulsified

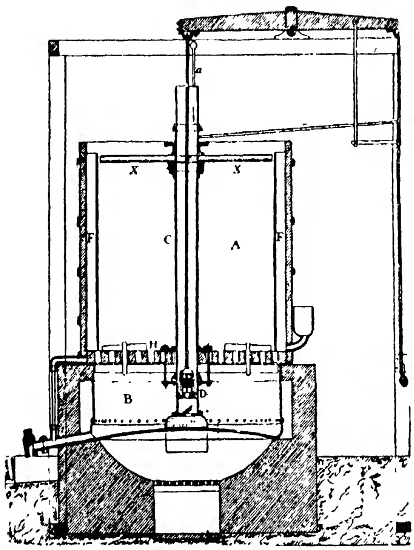

FIG. 110.—Apparatus of Berthollet.

by a long-continued boiling in alkaline solutions. On the other hand, cotton-wax is readily soluble in soluble (or sulfonated) oils, such as Turkey-red oil, which accounts for the fact that cotton may be quickly wetted-out by working in a solution of such an oil.

[7] Knecht and Allan (*Jour. Soc. Dyers & Col.*, 1911, p. 142) have made a very complete study of the wax obtained from the raw cotton fiber. The wax was obtained by extracting raw cotton in a Soxhlet apparatus, first with light naphtha and then with benzene, thus obtaining the product in two fractions. The first product was an odorless, dull yellow substance closely resembling beeswax in texture and fracture. By repeatedly extracting this product with boiling alcohol (96 percent) an insoluble wax of a glassy appearance was left; it had a melting point of 78° C. and an iodine value of 11.28. The portion soluble in alcohol was more plastic, with a melting point of 62°C. and an iodine value of 33.22. On heating the wax for some time with a semi-normal solution of alcoholic potash under a reflux condenser it was only slightly saponified, but by using Leffman's process with semi-normal glycerin-caustic soda solution it was found to contain 47.5 percent of unsaponifiable matter with melting point of 67°C. On acetylating there were obtained two hydrocarbons in a crystalline form, one with melting point of 68.1°C. and giving on analysis an empiric formula of $C_{31}H_{64}$, corresponding to hentriacontane, and the other with a melting point of 70°C. and an analysis corresponding to dotriacontane or dicetyl, $C_{32}H_{66}$. By separating and acidifying the saponified part of the wax a small amount of glycerin (0.21 percent) was obtained, also a slight quantity of a fatty acid with melting point of 74.4°C. (apparently cerotic acid), together with some stearic and palmitic acids. The second fraction of the wax obtained in the benzene extraction was a dark green granular mass with a melting point of 68°C., acid value of 4.03 and saponification value of 83.3. The unsaponifiable matter gave 33.35 percent of a reddish brown sticky wax with melting point of 63.4°C. From the fatty acids obtained from the saponified portion of the wax there was obtained a small quantity of a crystalline acid with melting point of 70.8°C. and apparently corresponding to melissic acid.

Analysis of cotton-wax shows it to consist of the following:

	Percent
Carbon	80.38
Hydrogen	14.51
Oxygen	5.11

It fuses at 85.9° C. and solidifies at 82° C.; hence it bears a close analogy to both cerosine (sugar cane wax) and carnauba wax.

Knecht,[8] by exhaustively extracting raw Egyptian cotton with benzene, obtained 0.47 percent of crude cotton-wax resembling beeswax in appearance and consistency. On treatment with naphtha the crude wax was separated into two constituents, cotton-wax A, amounting to 70 percent and soluble in the naphtha; and cotton-wax B, insoluble in naphtha. The first wax was of a pale color, with melting point of 66 to 67° C., and seems to consist for the most part of a true wax, though containing besides some free fatty acids and small portions of glycerides and hydrocarbons. The cotton-wax B was a plastic substance with melting point of 68° C. and containing very little free fatty acid. Texas cotton was found to yield 0.55 percent of wax soluble in benzene, while Bengal cotton gave only 0.38 percent of crude wax.

The coating of wax on the cotton fiber influences its spinning qualities to a considerable extent, as it requires, for instance, a rather elevated temperature to successfully spin fine yarns; this condition probably being necessary to soften the waxy coating on the fiber.[9]

Piest [10] has examined the extractive matters in cotton chiefly with reference to the point of view of the cellulose chemist. Raw American cotton linters gave the following results: wood-gum 1.32 percent; ether extract 0.74 percent; benzene extract 0.87 percent; petroleum ether extract 0.50 percent; absolute alcohol extract 1.23 percent; copper number 3.57; and ash 2.44 percent. The average figures obtained from a number of samples of normal purified cotton for nitration were: wood-gum 0.65 percent; ether extract 0.18 percent; carbon tetrachloride extract 0.19 percent; alcohol extract 0.35 percent; copper number 0.95; and ash 0.11 percent. The extract of cotton approximated to Japan wax in its melting point, saponification and iodine values.

Knecht [11] states that the question as to the fate of the cotton-wax in the bleaching process has been discussed from the theoretical point of view *ad nauseam*, but from the behavior of the wax towards a semi-

[8] *Text. Inst. Jour.*, 1911, p. 22.

[9] From spinning tests conducted on a large scale with Egyptian cotton deprived of its wax it has been shown (Knecht, *Text. Inst. Jour.* 1911, p. 22) that the dewaxed material behaves very badly in the drawing and spinning processes, giving an excessive amount of waste, irregular results, and showing a tendency to adhere to the rollers. In producing fine counts great trouble was experienced and breakages were very frequent. When used as a warp in the loom the dewaxed yarn was also troublesome on account of breaks. From actual tests it was found that the yarns spun from the dewaxed fiber were about 25 percent weaker than those spun from ordinary cotton. On the other hand, the extraction of the wax from ordinary yarn after spinning increased the strength by 13 percent, while the addition of 2 percent of paraffin wax to the extracted yarn decreased its strength again by 33 percent. Hubner made dyeing tests on cloth made from dewaxed raw Egyptian cotton and found that the direct dyes gave lighter shades on the dewaxed cotton than on the ordinary, whereas Methylene Blue and certain other dyes gave darker shades.

[10] *Zeit. angew. Chem.*, 1912, p. 396.

[11] *Jour. Soc. Dyers & Col.*, 1911, p. 145.

normal alcoholic potash solution it would seem scarcely likely that any saponification can take place in the alkaline treatment to which cotton goods are subjected by boiling in the kier. That the fatty acids present in the crude wax are readily removed by boiling with soda ash or caustic soda is only what would be expected, and it is just possible that the soap thus formed will remove some of the wax as an emulsion. But that the whole of the wax or anything like it is not removed by the

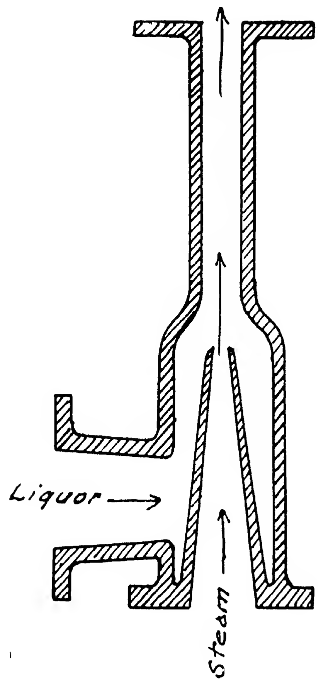

FIG. 111.—Showing Principle of Steam Injector.

ordinary kier treatment is shown by the results on gray Egyptian yarn, in which the "crude" wax was estimated before and after the kier treatment by extraction in a Soxhlet with benzene. (1) Boiling for 4 hours with soda ash at 4° Tw. removed 30 percent of the total wax present; (2) boiling for 4 hours with caustic soda at 2° Tw. removed 28 percent; (3) boiling for 20 minutes with caustic soda at 2° Tw. and 5 percent of soap (on the weight of the cotton) removed 45 percent; (4) using same mixture as (3) but boiling 4 hours, removed 64 percent; (5) boiling for 4 hours with caustic soda at 2° Tw. with the addition of resin soap removed 73 percent.

7. Fatty Matters.

The fatty acid present in cotton has been found to be identical with margaric acid. According to Schunck, American cotton contains about 0.84 percent of fatty matters, whereas East Indian cotton contains only

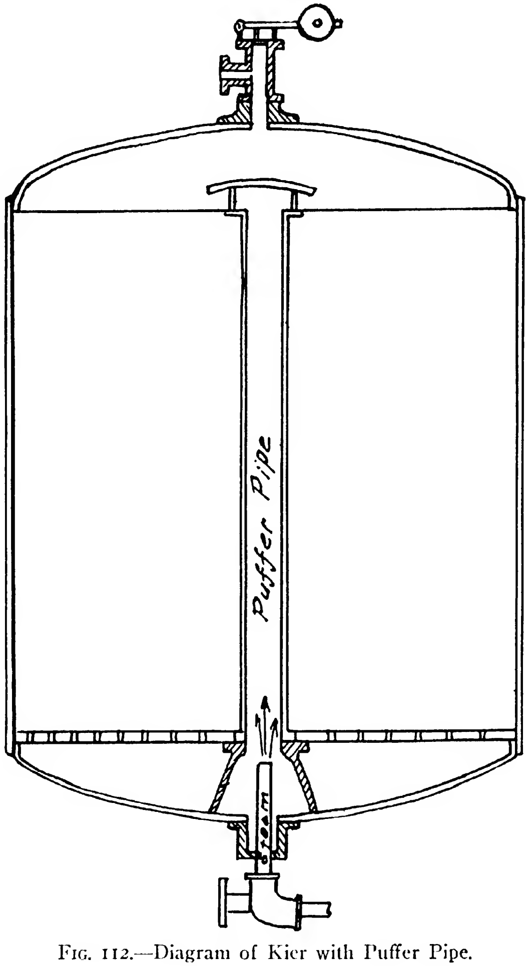

FIG. 112.—Diagram of Kier with Puffer Pipe.

0.337 percent. This probably accounts for the fact that the latter cotton is much harsher than American cotton.

8. Cotton-Oil.

Cotton-oil found in the fibers of raw cotton is apparently identical with cotton-seed oil, and is no doubt derived from the seed to which

the fiber is attached. In the ginning of the cotton some seeds become crushed and thus contaminate the fiber with more or less oil.

Cotton yarns and cloth sometimes contain other oils than the foregoing, such oils being intentionally added for the purpose of softening the fiber, or as an ingredient in the sizing materials used in yarns to enhance their weaving qualities. Tallow and cocoanut oil are largely used for these purposes and there may be present at times as much as 10 to 15 percent of such fatty matters in the cotton.

9. Albuminous Matters.

Albuminous matters are present in raw cotton to only a slight extent. These substances are nitrogenous in character, and doubtless consist of protoplasmic residues. The external cuticle and the wall of the inner canal of the fiber appear to be of an albuminous nature. The amount of nitrogenous matter present in cotton may be determined by

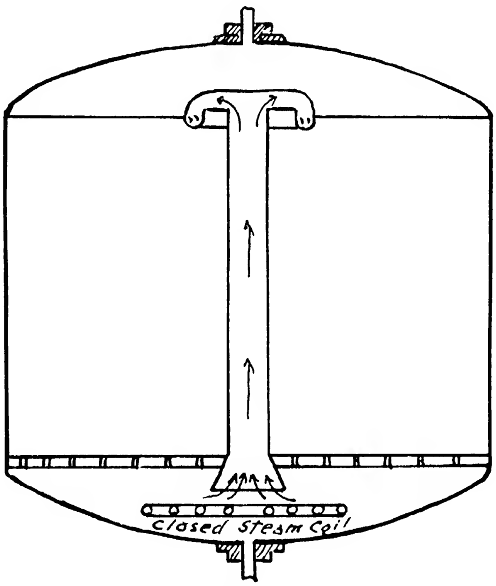

FIG. 113.—Showing Circulation Produced by Steam Coil.

Kjeldahl's process, as follows: 5 grams of cotton material are chopped up and heated in a flask with 30 c.c. of concentrated sulfuric acid and 2 grams of potassium permanganate. This treatment results in a complete decomposition of the nitrogenous matter with the liberation of ammonia, which immediately combines with the sulfuric acid present to form ammonium sulfate. An excess of caustic soda solution is now carefully added, and the solution boiled. This results in the liberation

of free ammonia as a gas. The latter is passed into a definite volume of 1/10 normal sulfuric acid solution, and the excess of acid not neutralized by the ammonia is subsequently titrated with 1/10 normal caustic soda solution, using Methyl Orange as an indicator. The amount of sulfuric acid neutralized measures the quantity of ammonia formed, which in turn determines the amount of nitrogen present in the original cotton. The quantity of nitrogen so obtained multiplied by the factor 6.4 gives the amount of nitrogenous matter present as an albuminoid.

The amount of nitrogen present in different varieties of cotton is given by Bowman as follows:

Cotton	Percent Nitrogen
American	0.30
Sea-island	0.34
Bengal	0.39
Rough Peruvian	0.33
White Egyptian	0 29
Brown Egyptian	0 42
Mean	0 345

From this it would seem that the amount of albuminous matters present is fairly constant in different varieties of cotton. According to analyses by Schindler [12] raw Egyptian cotton gave 0.25 percent of nitrogen. By boiling the cotton for 8 hours with caustic soda solution the amount was reduced to 0.064 percent. Schindler also states that if we assume the nitrogen in raw cotton to be present in the form of albuminoids, the amount of the latter would be about 1.6 percent. As Schindler's determinations related only to brown Egyptian cotton, Knecht has given some figures for other varieties of cotton as follows: American (gray yarn) 0.138 percent nitrogen; Texas (raw, cleaned) 0.150 percent nitrogen, and red Peruvian 0.280 percent nitrogen. It is evident, therefore, that American cotton contains less nitrogen than Egyptian or Peruvian.

It is likely that in the process of bleaching most of the albuminous matter is removed from the cotton fiber.[13] Haller has shown that bleached cotton is not tinted so deeply as raw cotton with an acid solu-

[12] *Jour. Soc. Dyers & Col*, 1908, p. 106.

[13] Knecht and Hall (*Jour. Soc. Dyers & Col*, 1918, p. 220) in experiments relating to the removal of nitrogenous matter from raw cotton in a single treatment, showed that boiling at atmospheric pressure for 6 hours with a 2 percent caustic soda solution removed about 80 percent of the total nitrogen; boiling with lime for 12 hours removed about 38 percent. but this was increased by subsequent souring to 53 percent Hot soaping removed only about 18 percent. By using yarn originally containing 0.248 percent of nitrogen and boiling under 35 lbs. pressure the following results were obtained:

Process	Proportion of nitrogen remaining, percent.
Raw cotton	100.0
After lime boil	54.0
After sour	40.5
After caustic boil	27.1
After sour	26.8
After bleach liquor	6.7
After sour	5.8

It would be interesting to have experiments conducted on actual mill samples on yarns treated with the usual caustic soda boil and followed by the various successive steps of the rest of the bleaching processes.

tion of Safranine, and he concludes that this is due to the albuminous matter acting as a mordant for the dyestuff.

Practically nothing is known of the chemical constitution of the albuminous bodies present in raw cotton, but they are probably similar

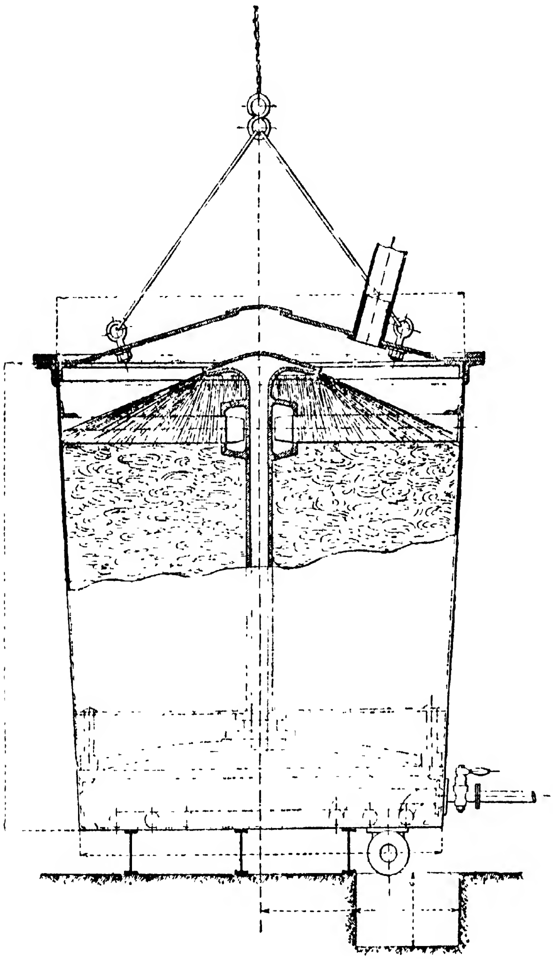

FIG. 114.—Open Type Kier with Vomit Pipe.

in composition and properties to the general class of proteoids. The fact that they contain an amino group (NH_2) and are capable of combining with chlorine to form bodies known as *chloramines* is interesting

as such a reaction may have some importance in the reactions involved in the bleaching of cotton.[14]

10. Coloring Matter in Cotton.

Coloring matter is present to a small extent in cotton and gives the fiber a slight yellowish brown tone. In some varieties such as brown Egyptian and Nankin cottons, the color is quite noticeable. It is a common opinion that the brownish colored cottons contain more iron than lighter colored varieties. This, however, is erroneous, as the ash of dark colored cottons does not contain a greater proportion of iron. The coloring matter is altogether an organic pigment.

The coloring matter of raw cotton consists of two organic pigments, the one soluble in alcohol, and the other dissolved only by boiling alcohol. According to Schunck[15] the composition of these bodies from Nankin cotton is as follows:

	A. Soluble in cold alcohol. Percent	B. Insoluble in cold alcohol. Percent
Carbon	58.22	57.70
Hydrogen	5.42	5.60
Nitrogen	3.73	4.99
Oxygen	32.63	31.71

The coloring matter of cotton is insoluble in water, and only partially soluble in alkaline or acid solutions. By the action of oxidizing agents it is either destroyed or changed to a soluble colorless compound. It is not so easily attacked by reducing agents.

There is a peculiar variety of peeler cotton known as *"blue bender"* cotton. The fiber is characterized by a bluish color which cannot be bleached out by the usual methods employed for the bleaching of ordinary cotton. It receives its name from occurring in the "bends" of the Mississippi River Valley. The exact nature of the color and the cause of its formation in this variety of cotton are not known. By some it is supposed that the defect arises from the plant being touched by frost too early, while others assume that the cause is to be found in some ingredient in the soil. Outside of its defective color and resistance to bleaching, the appearance and quality of the fiber are otherwise unimpaired.

11. Mineral Matters in Cotton.

Mineral matters exist in raw cotton in two forms. In the first place there is always more or less dust and sandy matter adhering as dirt to the surface of the fiber. The character and amount of this impurity vary much with the quality and geographical distribution of the cotton. In the second place, there is a certain amount of mineral matter

[14] Trotman and Thorp are of the opinion that the incomplete removal of nitrogenous matters in boiling-out not only makes the fiber resist the subsequent action of the bleach liquors, but is directly objectionable, owing to the power which proteids have of forming chloramines by the absorption of chlorine. The importance of this factor, however, in the boiling-out and bleaching of cotton cannot be assumed as yet to have been definitely established, and is only a matter of unsubstantiated opinion which should receive careful investigation before being accepted in the category of scientific fact.

[15] *Chem. News*, 1886, p. 118, 1874, p. 5.

in the fiber itself as an integral part of the cell and its constituents. The amount of mineral matter existing as adhering dirt will generally be from 1 to 5 percent and the amount of mineral matter as a constituent part of the substance of the fiber will be from 1 to 1.25 percent. The first kind of mineral matter is practically all removed from the cotton in the preliminary processes of its manufacture when it passes through the dusting and cleaning machines and cards. The mineral matter of the second kind is removed almost entirely by boiling-out and bleaching. The following tests by the author show the influence of these operations on the mineral content of the fiber:

	Mineral Matter as Ash, Percent
Carded Peeler 24/1 yarn raw	1.12
Boiled out 3 hrs., 12 lbs. pressure, with caustic soda and soluble oil	0.36
Bleached with chloride of lime and soured with sulfuric acid....	0.12

The amount of ash or mineral matter in bleached cotton is a good indication of the character and quality of the bleach as will be shown when the testing of bleached cotton is considered.

12. **Motes or Shives.**

Motes are the dark colored specks which are to be observed in all samples of raw cotton, whether in the loose state or manufactured into yarn or cloth. Combed cotton yarns will naturally have much less motes than carded yarns. These motes are small pieces of cotton-seed hulls and broken leaf particles which adhere to the fiber and are retained in the yarn and cloth. They contain oily matter, tannin, and besides considerable dark brown coloring matter, and are very resistant to the action of the bleaching processes. They can only be gotten rid of by a very thorough boiling-out with caustic soda or lime and subsequent bleaching with hypochlorites; but if the boiling-out has not been thorough, even severe subsequent bleaching will not suffice to decompose the motes. Material made from low-grade cottons and containing large quantities of persistent motes are sometimes treated with warm (100° to 120° F.) hypochlorite liquors.

As the seed particles, of which the motes are in most part composed, contain considerable amounts of tannin and oil, they may lead to certain defects in finishing. When cloth containing these motes is passed under great pressure through calender rolls the oil and tannin are squeezed out and form a small spot around the mote. When this comes in contact with iron a bluish or violet color is developed.

The destruction and removal of the motes is one of the most difficult problems with which the cotton bleacher has to deal.

13. **Sizing Materials.**

Besides the natural impurities to be found in raw cotton, there will also be present in cotton cloth various sizing materials, usually with starch as a basis. Warp yarns intended for weaving nearly always have to be sized with some variety of agglutinate in order to lay the fuzz of superficial fibers on the surface of the yarn, and also to give added strength and solidity to the yarn so that it may resist the wearing

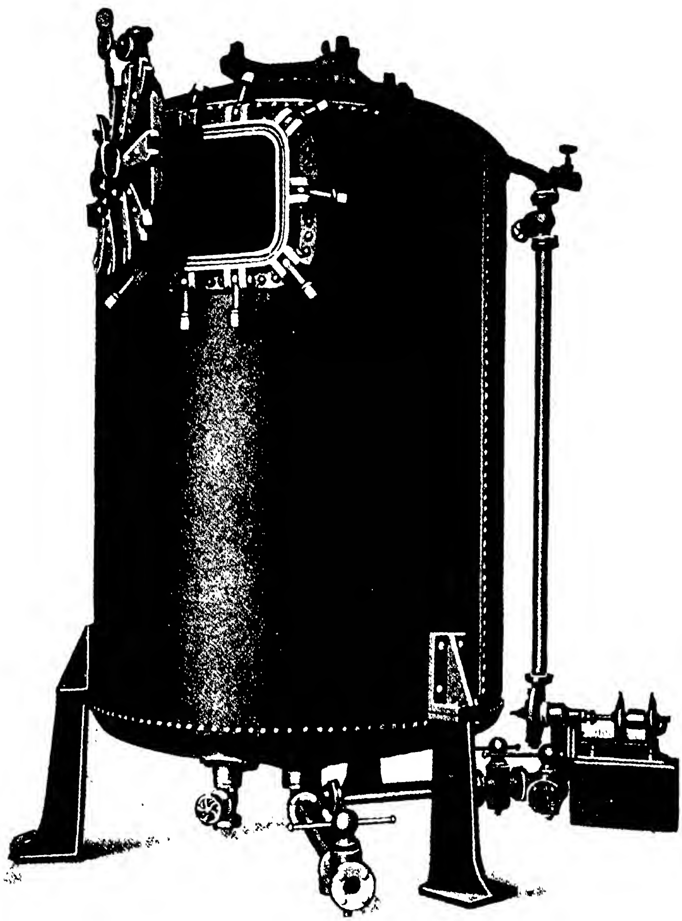

Fig. 115.—High Pressure Kier for Loose Cotton.

action of the shuttle in weaving. In the bleaching of cotton cloth these yarn-sizing materials have to be removed in the boiling-out process, either by treatment with alkaline liquors or with a malt preparation which will convert the starch into a readily soluble product.[16]

[16] Mueller (*Bull. Soc. Ind. Mulh*, 1909, p. 79), has made a detailed study of the removal of size from cloth in cotton bleaching, and as a result of a comparison of the material turned out from a number of bleach works, he concludes that the most important factor in the removal of the size is the duration of the lye boil. Different methods of bleaching when properly carried out appear to yield about equally good results. An acid steep in dilute sulfuric or hydrochloric acid does not seem to be very efficacious in the removal of the sizing materials, and the most efficient and rapid method for the removal of the starch and such-like bodies from the cloth is a treatment with a malt extract or enzyme.

Chapter XII.

The Boiling-out of Cotton *(Cont.)*.

1. General Theory of Boiling-out.

The scouring of cotton is generally referred to under the name of "boiling-out," and it has for its purpose the removal of the waxy matters from the fiber. This is usually done by boiling the cotton with dilute solutions of alkalies. The scouring of cotton may be for two purposes: (a) for removing the waxy coating of the fiber so that the cotton will readily absorb solutions of dyestuffs, etc.; this is termed "wetting-out" the cotton, and is generally required as a previous treatment to all dyeing and mordanting operations; (b) for removing as completely as possible all the impurities on the fiber so as to allow of a good clear white color being obtained by subsequent bleaching. This latter process is termed "boiling-out," and is naturally more thorough and severe than the simple wetting-out process.

If raw cotton is placed in water it will persistently float on the surface by reason of the water-repellent quality of the waxy matters with which the fiber is coated. If boiled for a long time in water the fiber will gradually become wetted and will eventually sink. If boiled in a dilute solution of soda ash, caustic soda, or other alkali, the wetting-out of the fiber will occur much more rapidly. Solutions of soaps and soluble oils will also wet-out cotton quite rapidly and even more effectively than alkalies.

As a process preliminary to bleaching, the boiling-out of cotton must be very thorough. In fact, it may be said that the success of bleaching cotton depends most largely on proper boiling-out; therefore the complete cleansing of the fiber before treatment with the bleaching solutions proper is very essential.

There are two general processes employed for the boiling-out of cotton preparatory to bleaching, and these may be called (a) the lime boil and (b) the soda boil. In the first process the chief agent employed is milk of lime, whereas in the second process a solution of caustic soda is used. In both cases the cotton is boiled in closed kiers under moderate pressure for a number of hours. The lime boil is by far the more complicated as it requires not only treatment with milk of lime, but also succeeding treatments with soda ash, resin soap, and intermediate sours, or treatment with acid. The soda boil is much simpler, being comprised in one operation and requiring only 8 to 12 hours for its completion. The lime boil, on the other hand, requires from 2 to 3 days. In most bleacheries the lime boil is gradually being

superseded by the soda boil, for when the latter is properly conducted it apparently gives as good results as the older and more complicated process.

2. Effect of Alkalies on the Cotton Fiber.

As the boiling-out operation has to do with the action of alkalies on cotton and the impurities therein it is well to have a clear understanding

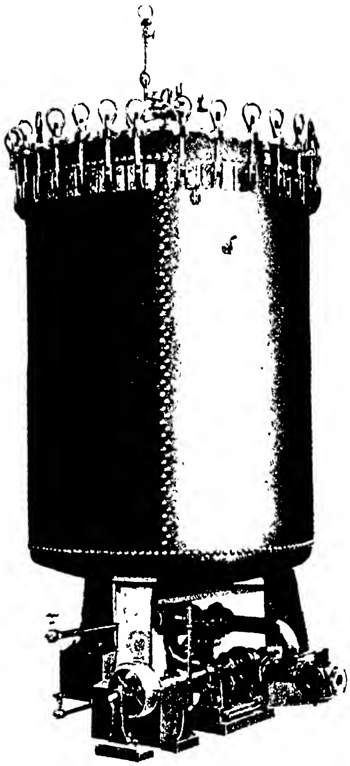

Fig. 116.—High Pressure Kier for Yarns.

of the effect produced by these chemical agents on the cotton fiber. As already pointed out the pure cotton fiber consists of a form of cellulose and this material is quite resistant to the chemical action of alkalies. Dilute, or even rather concentrated, solutions of the weak alkaline salts, such as borax, sodium phosphate, soap, etc., have practically no effect on cotton. Also dilute solutions of caustic alkalies and caustic lime have no effect on the fiber if not in the presence of air. From cold solutions of these alkalies cotton absorbs some of the alkali-base or

alkaline earth base and retains it with such firmness that it is difficult to wash it out. Thies has shown that thick layers of cotton really filter out the alkaline base from solutions of caustic soda or milk of lime. A test was made with 100 gms. of boiled-out, dried cotton yarn; this was steeped for 10 minutes in 1,500 c.c. of cold 1/5 normal solutions of soda ash and caustic soda respectively. Then the strengths of the alkaline solutions were determined, and it was found that that of the soda ash solution remained unchanged but the strength of the caustic soda solution had diminished in the ratio of 10:9.4. It was also found that on equally centrifuging the wet skeins and then rinsing with water the soda ash residues were much more quickly removed than those of the

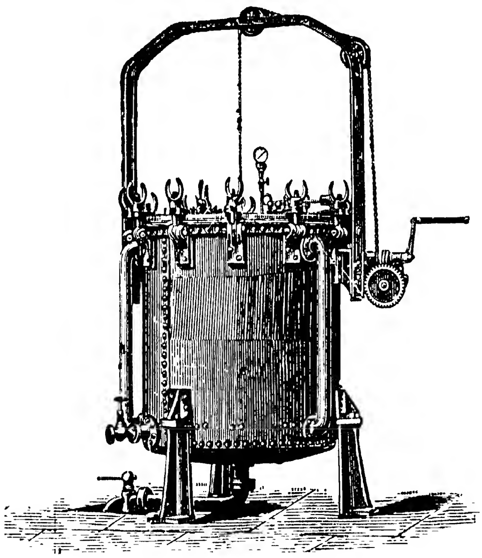

FIG. 117.—Small Kier for Skeins.

caustic soda. In other words it would seem that cotton cellulose combines in some form with caustic alkalies. It is presumed by some that a definite body known as alkali-cellulose ($2C_6H_{10}O_5.NaOH$) is formed, but this has yet to be accurately established. This alkali-cellulose, however definite or indefinite may be its chemical structure, is rather sensitive to atmospheric oxidation and also to high temperatures. On this account the simultaneous action of caustic alkali and air is apt to be injurious to cotton. In this connection, however, the concentration of the caustic lye is important. According to Thies, a caustic soda solution of 1 to 2 percent strength even with air in a kier has no injurious effect, whereas a caustic soda solution of 4 to 5 percent strength under the same conditions has a very noticeable weakening

action on the cotton. Consequently it may readily be understood that when caustic soda solutions of such strength are employed for boiling-out care should be taken to remove all air from the kier.

Highly concentrated solutions of caustic soda effect the so-called mercerizing action on the cotton, whereby the fiber shrinks in length and becomes distended laterally; this effect is brought about better by cold solutions than by hot liquors, and it is not produced by strong liquors of milk of lime. In boiling-out cotton solutions of caustic soda of sufficient strength to produce mercerization are never used, as it requires a strength of about 30° Tw. to give this effect. It may be possible, however, that when strong stock solutions of caustic soda are added freshly to the kier in starting a boil-out, the fiber may come in contact with such solution of sufficient concentration to produce some mercerizing effect. On this account it is bad policy to add the strong caustic liquor directly to the kier, but the diluted solution should be used. This is particularly true if the cotton or the caustic lye is hot, as under such conditions there is danger of the formation of oxycellulose which causes a tendering and discoloration of the cotton.

The question as to whether the dilute hot caustic lyes employed in boiling-out have any weakening action on cotton has been much debated, and the matter is still somewhat in a state of suspense. So many conditions and variations enter into the problem that it is difficult to compare the results of different investigators. Kind [1] has shown that cotton yarn scoured with benzene has a higher tensile strength than when boiled-out with caustic soda. The action of the alkali in connection with the hardness of the water is also to be considered, as lime and magnesium salts may be precipitated in the fiber, thus causing it to become harsh in feel and perhaps weaker in strength. The use of very soft water in this connection would therefore be beneficial.

3. Use of Lime.

Some bleachers claim that the use of lime is dangerous; that there is liability of "burning" or tendering the goods in spots; but this is usually the result of careless working and the leaving of particles of the lime in the cotton to be dried therein. If oxidizing agents in general, and air in particular, are excluded, the action of lime does not appear to sensibly diminish the strength of cotton, whether the treatment is carried out cold or hot. If oxidizing agents, however, are present a considerable deterioration in the strength of the fiber will be noticed. The use of lime, on the other hand, is preferred by some as it is somewhat cheaper than the other alkalies, and it is also said that the goods afterwards preserve their white color better in the shop and show less tendency to become yellowish, but if the other bleaching operations are properly conducted there is no real reason for this being so whatever alkali is employed. When boiling-out cotton with lime, it is best to follow with an acid bath in order to dissolve off all particles of lime which otherwise might adhere to the fiber and cause a tendering of the goods.

[1] On the action of acids and alkalies on cotton and linen, see *Deutsche Färber-Zeit.*, 1909.

Scheurer in an exhaustive paper before the Industrial Society of Mulhouse[2] arrives at the following conclusions with respect to the action of various alkalies in the bleaching of cotton and while there has been much progress in the methods of boiling-out and bleaching since that time, nevertheless the conclusions herein stated are still of very pertinent interest to the modern bleacher. On account of the protective influence exerted on the natural pigment of the fiber by the fats and waxes it is very important that saponification take place

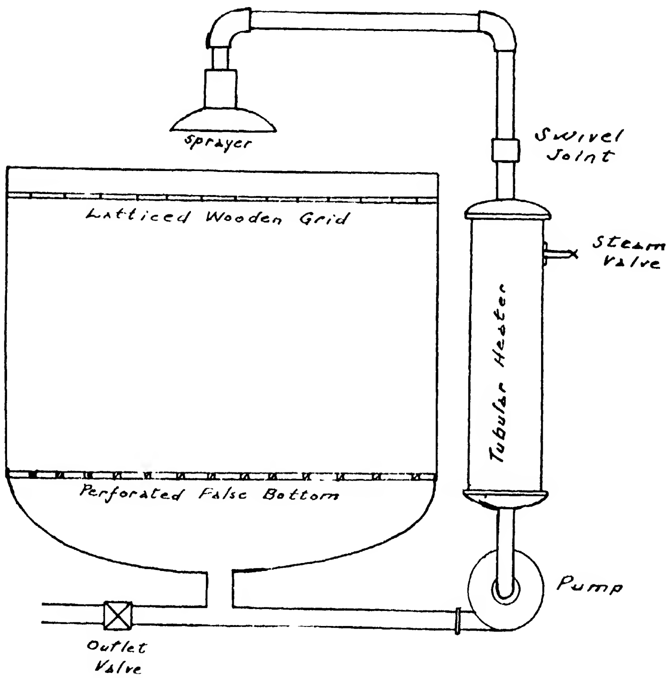

FIG. 118.—Diagram of Open Type Kier with Pump.

as rapidly as possible. When the lye boil with soda ash is not preceded by a lime boil, the results are not as good as when caustic soda is used. The lye boil with soda ash, preceded by a lime boil, gives better results than a caustic soda lye boil preceded by a lime boil. The lime boil is the basis of the bleaching with soda ash. In order to obtain a uniform white, the saponification of all the oily matters in the cotton must precede the destruction of the coloring matter, and it has been found that not only have the alkalies and bleaching liquors more effect on the coloring matter after the oil has been removed, but also the sun's rays. The fatty matters to be found in cotton cloth include not

[2] *Jour. Soc. Dyers & Col.*, 1889, p. 43.

only those natural to the fiber, but also those acquired during the processes of manufacture, such as olive, cotton-seed, palm, rape-seed and other vegetable oils, as well as tallow; these are all more difficult to saponify than the natural wax, especially tallow. From a series of experiments using alkaline solutions at 100° C., it was found that caustic soda saponifies the fats occurring in cotton in half the time that soda ash does; there is also little difference between the time taken by caustic soda of a strength of 5 gms. per liter and of 10 gms. per liter to saponify the fats. On the contrary, there is a great difference in the case of soda ash, and also in the case of a mixture of caustic soda and resin. The mixture of soda ash and resin does not saponify the fats any quicker than without resin. In the lime boil (using 10 gms. per liter of caustic lime) the natural fats were saponified in 6 hours while it required 12 hours to saponify tallow. Baryta water gave a saponification but it was not complete. By heating under pressure at a temperature of 120° C., caustic soda, with or without resin, saponified the natural fats in 4 hours. Without resin, tallow required 12 hours for saponification, while with resin 8 hours was sufficient. Caustic lime of 10 gms. per liter under pressure but without circulation saponified the natural fats in less than 2 hours, and tallow in less than 4 hours. Hence, the conclusion in this respect was that to obtain a rapid and complete saponification, it is necessary to use the lime boil or the caustic soda and resin boil. Barytes also appears to act as a solvent for the coloring matter of the fiber, for cotton boiled with it was much clearer than when boiled with lime. The addition of larger amounts of resin than 2½ gms. per liter with the caustic soda boil does not hasten the saponification.

4. Alkalies and Oxidizing Agents.

Caustic soda acts very energetically in the removal of the various waxy and resinous matters in cotton and hence it requires less time in boiling-out; but care must be had in its use, especially with reference to allowing the cotton to be exposed to the action of the air while saturated with the hot lye. The action of alkalies in general, and of caustic soda in particular, on cotton commands attention by reason of the increased use of this latter body for boiling-out of cotton previous to bleaching. Even in cold, dilute solutions, caustic soda acts rapidly on cotton, and in fact on cellulose fibers in general, and enters into combination with them, without, however, causing any reduction in the tensile strength of the fiber. Mills found that cellulose absorbs 0.02 percent of caustic soda after 3 minutes immersion, and according to Vignon, the amount of heat disengaged during this reaction is 0.58 calory per 100 gms. of cotton. This chemical reaction explains, to some extent at least, the reason why caustic soda dissolves with such readiness the impurities present in cotton and linen. As to the effect of temperature, it may be said that even at 120° C. caustic soda does not seriously deteriorate the strength of cotton, provided the strength of the solution is not over 1 to 2 percent and that no oxidizing agents are present. If the solution, however, contains more than 3 percent

of caustic soda, the cotton will rapidly dissolve, and under the conditions given, the loss in weight will reach 12 percent when a pressure of 14 pounds is maintained. Even dilute solutions of caustic soda in the presence of air and at temperatures above 100° C. will rapidly attack cotton, producing an oxidation of the cellulose. Weber[8] gives some interesting facts concerning the tendering of cotton by alkalies in the presence of oxidizing agents. In his experiments, cotton was exposed for 6 hours to an alkaline treatment in connection with oxygen or air, boiling baths containing 5 percent of various alkalies and alkaline salts being used. The following is a summary of his results:

With 5 percent solutions of	Loss percent of tensile strength			
	Oxygen	Steam and Oxygen	Air	Steam and Air
Caustic soda	11.05	17.3	5.2	9.2
Caustic potash	22.8	29.8	8.4	11.7
Sodium carbonate	8.2	10.1	3.9	5.4
Potassium carbonate	13.7	16.4	5.3	2.8
Borax	5.9	6.8	2.2	2.8
Sodium phosphate	3.1	3.5	2.05	2.3

Caustic soda under such conditions will cause a rapid deterioration in the strength of the cotton, as in the presence of air the soda lye converts the cotton into oxycellulose, a brittle and friable substance. After scouring with caustic soda, the washing should also be thorough, especially if the material is afterwards to be exposed to the air before other operations have had a chance to remove the lye. Sodium carbonate acts on the impurities of cotton in the same manner as caustic soda, only its action is slower. There is also less danger of injuring the fiber when using soda ash; and again in the case of bleaching fabrics containing colored yarns woven with white, it is always best to use soda ash for scouring, as caustic soda, even in dilute solutions, will destroy many colors which much stronger solutions of soda ash will not injure. A mixture of soda ash and caustic soda, known as "salt-of-soda," is frequently used by bleachers for scouring cotton. The general proportion of this mixture is 15 to 20 percent of caustic soda and 80 to 85 percent of soda ash. Instead of using sodium compounds the corresponding potassium compounds may be employed, but these are seldom used as they are no more efficient and they are much higher in price. Sodium sulfide has been found to be a very efficient scouring agent for cotton, but on account of its destructive action on metallic pipes and other fittings, and also as it is decomposed by chlorine with the separation of sulfur in the fiber, it has not been directly available for bleaching purposes. All alkaline sulfides appear to be more active than caustic alkalies in dissolving the impurities from the cotton fiber. And as under proper conditions they have no injurious action on the cotton, they would appear well adapted for use in the boiling-out of cotton previous to bleaching; they are not of practical use, however, owing to their corrosive action on metal vessels, and to the fact that if not very thoroughly washed out of the

[8] *Jour. Soc. Chem. Ind.*, 1893, p. 118.

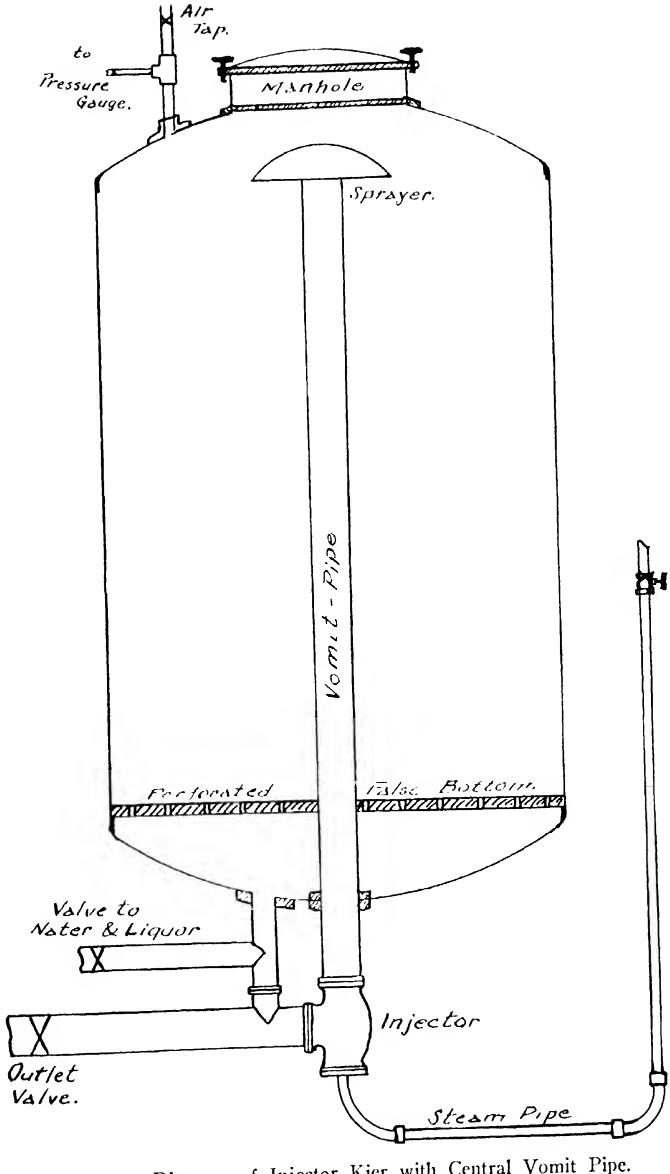

FIG. 119.—Diagram of Injector Kier with Central Vomit Pipe.

goods, the sulfides will react with the chloride of lime solution and thus cause loss of chlorine. Alkaline sulfides are also liable to act injuriously on cotton, especially if exposed to the air, unless considerable precautions are employed. Sodium bisulfite may be used for scouring cotton, as it readily acts on the foreign matters present. It is seldom employed by itself, but many bleachers add some of it to the soda lyes, the usual proportion being one part of sodium bisulfite to six parts of caustic soda.

5. Effect of Pressure in Boiling-out.

Besides the action of alkalies in the boil-out there must also be considered the effect of pressure. At the present time cotton is nearly always boiled-out in pressure kiers with suitable circulation of the liquor. With respect to the effect of pressure it may be said this is very necessary in the case of cotton containing a high proportion of motes and woody particles. Boiling without pressure will not decompose these highly resistant particles unless continued for an unduly long period of time, a condition which is liable to cause injury to the cotton.

With the usual caustic lyes employed it seems that pressures as high as 3½ atmospheres may be used without injury to the fiber; the customary pressure used, however, is about 12 to 15 pounds. The use of pressure in boiling-out considerably shortens the necessary time of treatment and also ensures a more uniform and thorough impregnation of the material. It is only on very clean combed yarns that it is possible to obtain a very thorough and complete boil-out without the use of pressure.

The degree of pressure most satisfactory for boiling-out varies with the size of the kier; for instance, in a small kier (for 1,000 lbs. of yarn) a good boiling-out may be given at about 8 pounds pressure in 2 to 3 hours, whereas a kier four times the size (for 4,000 lbs. of yarn) may require 15 to 25 pounds pressure for 8 hours.[4]

6. Requirements for Complete Boiling-out.

The time required in boiling-out for the complete saponification or emulsification of the fatty and waxy matter, as well as the other miscellaneous impurities accumulating during manufacturing processes and also including sizing materials, depends on the strength of the alkaline lye in the first place, also on the character of the alkali (particularly with regard to its hydroxyl ion concentration), as well as the temperature, pressure and nature of the circulation of the liquid. There must also be considered the emulsifying efficiency, or cleansing effect, of the lye. In regard to this latter action it may be remarked that soap and soluble oil are frequently added in conjunction with the alkali in the boil-out liquor, these materials being used principally for their general cleansing effect in giving an increased emulsifying efficiency to the scouring solution. This is particularly advantageous when mineral oil is to be removed from the cotton, as in this case

[4] *Oesterreichs Wollen und Leinen Industrie*, 1910, p. 500.

the scouring efficiency of the alkali is much increased by the addition of a small amount of soap or soluble oil (sulfonated, Turkey-red, or Monopole oil). The same thing is true as to the use of resin in the lye boil, this product forming a soap with caustic alkali that possesses high emulsifying properties.

The action of the caustic soda, or milk of lime, on the fatty matters in cotton is generally spoken of as saponification; that is to say, an action resulting in the chemical combination of the fatty matter with the alkali base to form a soluble soap. Just to what extent actual

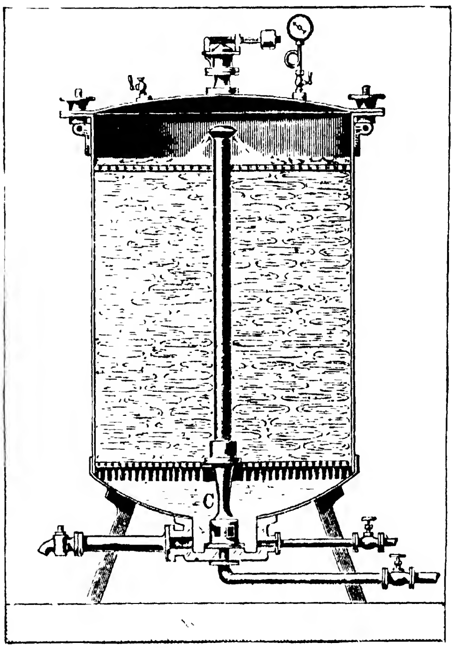

Fig. 120.—Kier with Inside Injector.

saponification takes place with the rather dilute solutions of caustic alkali employed is a question; there is probably more of an emulsification of the fatty matters than a real saponification. This view is also furthered by the fact that most of the natural greasy matter on the cotton is a wax rather than a fat, and waxes are not subject to the same character of saponification as the fats.

It might be argued from this that the use of a pure soap solution would be more efficacious as a boil-out medium than alkalies; but such does not seem to be the case, as the use of soap alone does not seem to be severe enough in its action. It must be remembered in this connection, also, that besides the fatty or waxy matters naturally pres-

ent in cotton, there are furthermore various albuminous substances present, which it is also the function of the boil-out to remove, and probably this requires a vigorous alkaline treatment. In addition to this, the cost of soap is much higher than that of caustic soda.

The effect of soluble oil in cleasing cotton in the boil-out is so effective as far as color goes in comparison with that of caustic soda alone that various attempts have been made to give cotton a partial bleach by this means without passing through a hypochlorite treatment. The process of G. Hertel,[5] for example, is to impregnate cotton yarn with Turkey-red oil, dry it, and then boil in a caustic soda lye for 6 hours under 2 atmospheres pressure, followed by thorough rinsing, souring, and soaping. In this manner it was claimed to be able to obtain a three-quarter bleach without the use of chlorine. While the result may have been fairly satisfactory the cost was too great owing to the large amounts of Turkey-red oil and soap that were required. Another method by G. Saget calls for the impregnation of the cotton with 8 percent of Turkey-red oil, drying, and steaming for 1½ hours under 7 pounds pressure, rinsing in hot water, and then boiling-out with lime.

Suggestions have also been made to add soluble oil to the milk of lime in a lime boil. The result of this, however, according to the investigations of Scheurer[6] is to cause oil spots to form in bleaching owing to the insoluble lime soap that is formed, therefore the process is to be condemned.

Knecht and Allan[7] in a detailed investigation of cotton-wax show that it is not saponified to any extent when boiled with a semi-normal solution of alcoholic potash, and therefore it would scarcely seem likely that any saponification can take place in the alkaline treatment to which cotton goods are subjected by boiling in the kier. That the fatty acids present in the crude wax are readily removed by boiling with caustic soda is no doubt true, and it is possible that the soap thus formed will remove some of the wax as an emulsion; but it has been shown by analysis of cotton before and subsequent to boiling-out that only a minor part of the wax is so removed. Knecht gives the following results of his experiments:

	Reagent	Hours Boiled	Percentage of Wax Removed
1	Soda Ash, 4° Tw.	4	30
2	Caustic Soda, 2° Tw.	4	28
3	Caustic Soda, 2° Tw. Soap (5% on wt. of cotton)	4 3½	45
4	Caustic Soda, 2° Tw. Soap (5% on wt. of cotton)	4 2	64
5	Caustic Soda, 2° Tw. With resin soap	4	73

In these tests the boiling-out was conducted without pressure.

[5] *Ger. Pat.* 75,435.
[6] *Mulhausener Berichte*, 1903.
[7] *Jour. Soc. Dyers & Col.*, 1911, p. 145.

7. Value of Soaps in Boiling-out.

As to the value of different soaps in the boiling-out of cotton this depends largely on the content and nature of the fatty acids from which the soap is made. In this connection it appears that resin soap,

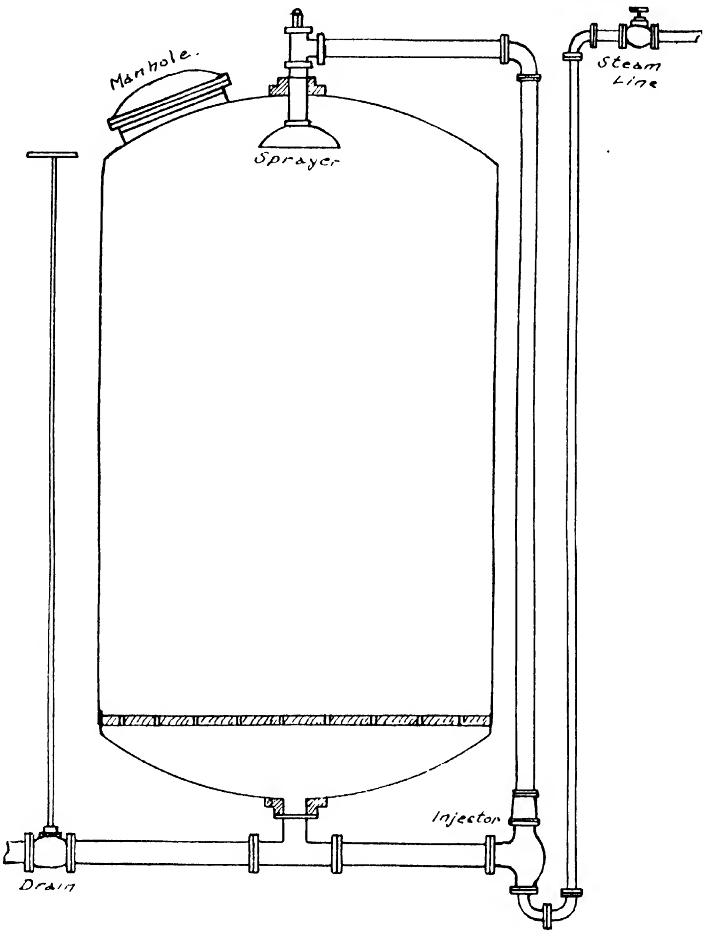

FIG. 121.—Diagram of Kier with Outside Circulator.

though not a fatty acid compound, is particularly efficacious. Acid soaps, such as Turkey-red oil, Monopole Soap, etc., give somewhat more stable emulsions, particularly in the case of fatty mixtures. These products also differ in their action from soap in that they do not give a precipitate with hard water. The use of ordinary soap as

an addition to the kier in boiling-out when hard water is employed results in the formation of an insoluble lime soap which may be absorbed by the fiber and become difficult to remove subsequently. This may lead to serious faults in bleaching which may not develop until some time after the goods are finished. It might be thought that as the soap is always used in the kier boil-out in connection with proportionately large quantities of caustic soda or soda ash, the formation of any lime soap would be avoided by the softening effect of the alkali on the water; but it must be remembered that in the boil-out the water is not separately treated and filtered so as to remove the lime compounds, but that the soap and the lime are being boiled up together under conditions which no doubt would lead to the formation of some lime soap notwithstanding the simultaneous presence of the alkali. It is true, nevertheless, that where a large excess of alkali is present the precipitated lime soap is for the most part decomposed or converted into the soluble double salt of lime-soda fatty acid compound.

8. Use of Volatile Solvents.

Another modification in the general scheme of boiling-out is the use of direct solvents for the fats and waxes. Benzine (or naphtha) and naphtha soaps have been suggested as additions to the kier liquor. Other solvents such as turpentine, phenol, aniline, carbon tetrachloride and similar bodies have been tried. These are usually emulsified with soap and used in that form. Certain proprietary compounds such as Tetrapol and Benzoform have been put forward as boil-out assistants. The defect in the use of any kind of volatile solvent, however, is in the fact that under the conditions of boiling-out the solvent is quickly evaporated and that it is a matter of conjecture as to whether it really has a chance to exert any solvent action at all.

9. Air as a Factor in Boiling-Out.

The influence of air in boiling-out is another factor to be considered. It has already been mentioned that the presence of air in the kier during the boil is liable to lead to the formation of oxy-cellulose and result in defective bleaching. Air may be present in the kier from several causes (a) the residual atmospheric air left after filling the kier; the kiers are never filled completely to the top, and besides there is a large quantity of air held in the cotton. This air accumulates at the top of the kier soon after the goods are heated, and it is customary to evacuate it through a valve supplied for this purpose. (b) The air introduced into the kier by the water and solutions used; cold water holds in solution an appreciable amount of air which is expelled on heating. (c) The air introduced with the steam.

The last, perhaps, is the most important item to consider, as the air from the first two causes is almost completely gotten rid of when the boiling of the kier is first started by opening the air-valve. The air that is introduced with the steam, however, is continually being

brought into the kier by the constant admission of the steam, and this air comes in contact with the goods at a high temperature and when saturated with the alkali. In this connection it is to be noted that caustic soda and lime behave differently in the kier. From ex-

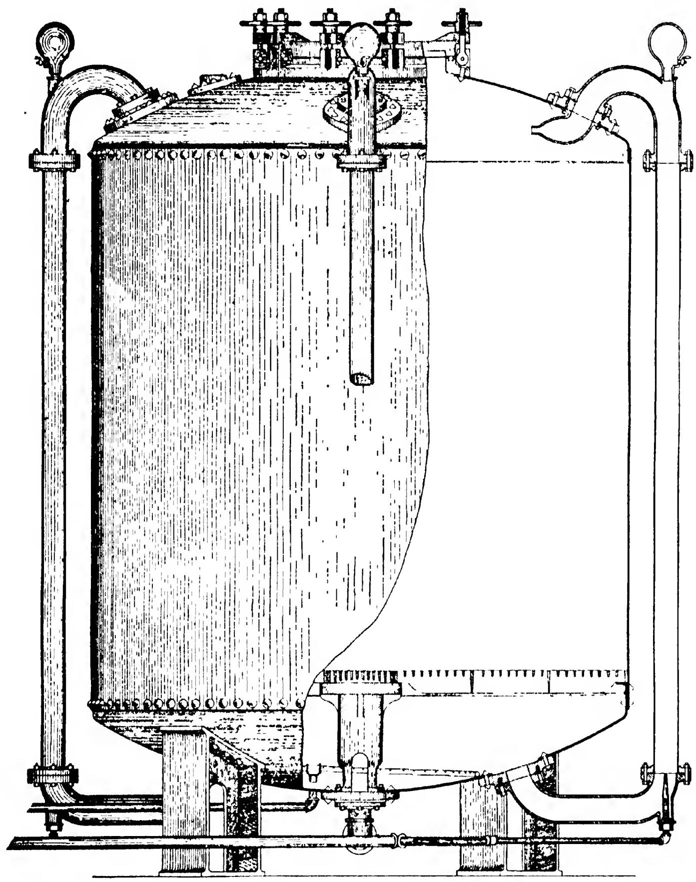

FIG. 122.—Allen Kier, Old Type.

periments conducted by H. Thies it was found that after 45 minutes of steaming of goods that contained no lime the oxygen of the air introduced by the steam was not absorbed; on the other hand when the treatment was made with goods containing lime practically all the oxygen was absorbed though the goods were not tendered. In using

caustic soda of the same equivalent strength as the lime no absorption of oxygen was noticed, but by increasing the strength of the caustic soda fivefold, it was found that all the oxygen was absorbed, and that the goods surrounding the central pipe of the kier admitting the steam were tendered and discolored. These experiments are significant and indicate that while with lime the air acts on the material, this action is slow and if any oxycellulose is formed with the cotton it is evenly distributed and causes no tendering, though it is more probable that with the lime the air acts on the impurities rather than on the fiber itself. With caustic soda at proper dilution the air has no action, but if the caustic lye becomes concentrated the action is rapid and destructive. Thies also showed that the kier liquor after the boiling has progressed becomes reducing in its action in the case of both lime and caustic soda. This reducing action being shown by the fact that samples of indigo dyed cloth became discolored, apparently by the reduction and solution of the indigo from the fiber. This action of the kier liquor, in fact, is now well known to bleachers who have to boil-out and bleach cotton goods that contain colored yarns. Thies sought to take advantage of this reducing action of the kier liquor by passing the goods through an old kier liquor previous to packing them in the kier, it being supposed that the reducing action of such liquor might prevent any bad effect due to oxidation by the air in the kier. Modern kier practice seems to indicate, however, that this is unnecessary. With the care that is now taken for the total expulsion of the residual air in the kier on first starting the boil, and the use of dilute caustic soda as the boil-out liquor, there does not seem to be any good reason to fear the effect of the air introduced by the steam.

The possible influence of the air introduced by the steam used in boiling, however, has been considered in the construction of special forms of kiers to obviate this objection. In the old Thies-Herzig kier and in the newer Walsh kier the construction is such that no steam comes in direct contact with the cotton and hence the tendency towards any formation of oxycellulose due to this cause is entirely avoided. The kier liquor is heated in an outside auxiliary boiler and circulated by means of a pump.

10. Removal of Starch in Boiling-out.

Of the several classes of impurities in cotton probably the one which is least affected by the ordinary process of boiling-out is the starch (or similar related product used for sizing the yarns). In the case of the lime-soda boil there is no doubt but that considerable starch is left undisturbed. With the caustic soda boil a larger proportion of the starch is removed. This problem has led to the suggestion of using an acid treatment on the goods previous to boiling-out for the purpose of converting the starch into an easily soluble product. For this purpose Thies recommended running the goods through a bath containing 10 gms. of sulfuric acid and ½ gm. of hydrofluoric acid per liter and then steaming for 20 to 60 seconds.

After this the goods are run through an alkaline kier liquor and into the kier for boiling. The use of acid in this connection, however, is dangerous, as when operating under practical mill conditions it is not always easy to avoid tendering the goods.

Another treatment for the removal of the starch which is perhaps even far more efficacious and at the same time unaccompanied by any elements of danger to the cloth, is to give the goods a preliminary treatment with a malt enzyme solution (such as Diastafor, Diax or Polyzime) which renders the starchy matters readily soluble. So successful has this method of treatment been found that it is now very extensively practised, as by its use it is possible to much reduce the severity of the alkali boil in the kier. The enzyme action not only solubilizes the starch but it also seems to render the pectin matters of the cotton fiber itself more amenable to the scouring effect of the alkaline liquors in the kier, giving a purer kier liquor and a cleaner cotton.

11. Determining Completeness of Boil-out.

There is a considerable difference of opinion as to just what may be considered a complete boil-out of cotton; that is to say, when is the boiling-out process to be considered as finished? What means are there of ascertaining if the impurities have been completely removed from the fiber? To what extent must these impurities be removed in order to have a good or a bad boil-out? These questions are naturally very pertinent ones, but apparently in practice they are not answered or even considered in any systematic manner, but the reliability of the boiling-out process is gauged by the quality of the final bleach after all of the operations of bleaching have been completed. Suggestions have been made by chemists to determine the completeness of the boil-out by some analytical investigation of the boiled-out goods, usually with a reference to the amount of fatty bodies still left in the goods.[a] Ambühl,[3] for instance, gives the following analyses of cotton yarn:

	Free Fat Percent	Fatty Acids Percent	Ash Percent
Gray yarn	1.0448	0.1359	1.6294
After boil-out	0.1761	0.0923	0.2230
After bleaching	0.0210	0.0433	0 0571

There is no doubt but that in all practical boiling-out of cotton there is some fatty matter still left in the material, and in the case of cloth it is doubtful if absolutely all the starchy matters of the size are removed. As to the proportion of removal of the so-called pectin bodies of the fiber there is no definite data on which to rely, and the same is also true perhaps of the nitrogenous or protein matters on the fiber. The textile chemists are perhaps more at fault in this matter than the practical operating bleacher, for it is really due to the failure or inability of the chemist to devise a satisfactory and practical method of testing boiled-out cotton in order to determine definitely the quality of the boil-out that the bleacher himself has had

[3] *Jour. Soc. Dycrs & Col.*, 1903, p. 256.

to fall back on the only practical test he knows of—that of finding if the final bleached article is of a satisfactory quality. There is a field here, however, for considerable chemical research in the study of the

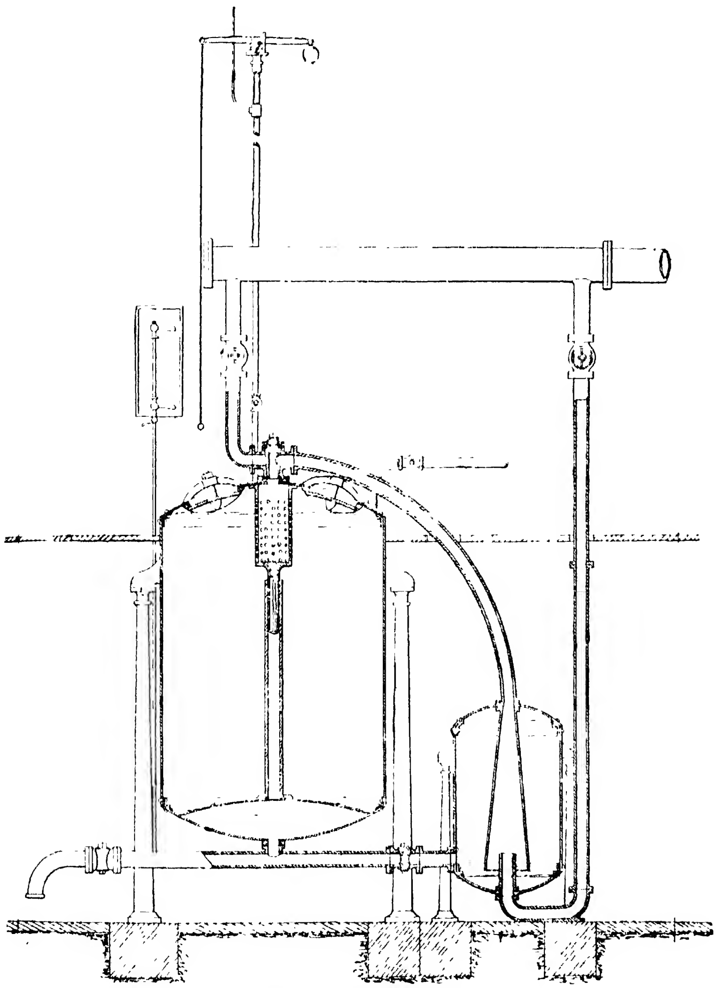

FIG. 123.—Taylor Kier.

operations of the boiling-out process and the development of a proper method of testing the quality of the boiled-out goods in order to check the character and completeness of the operation.

12. Boiling-out by Steaming.

Another feature in the general consideration of the boiling-out process is the use of a form of kier in which the cloth is not really boiled at all. Reference is here had to open-width method of boiling as practised, for instance, in the Mather-Platt kier. In this process the cloth is contained on two cylinders from which it is rolled back and forth during the treatment, being subjected to the action of steam under pressure while the fiber is impregnated with the alkali liquor. This is really a steaming operation rather than a boiling-out process, and the alkali liquor becomes concentrated on the cotton. Such methods of treatment, however, do not seem to have met with much practical success, for it appears that if the process is so conducted as to be made severe enough to remove satisfactorily the impurities of the fiber there is too much danger of the formation of oxycellulose and the consequent tendering and discoloration of the goods. The improved method of Thies-Herzig, however, in which the goods are subjected to the action of a steam and alkali foam free from air seems to have shown good results and has considerable practical application in Germany.

13. Use of Sodium Bisulfite.

Another variation in the matter of boiling-out is the use of sodium bisulfite in the kier. This is usually employed in connection with caustic soda and probably receives its suggestion in the matter of boiling-out cotton from the fact that bisulfite liquors are so extensively and efficiently employed for the cooking of wood-pulp in the preparation of paper fiber. The use of caustic soda in connection with the bisulfite, of course, results in the neutralization of some of the caustic soda and the consequent formation of some neutral sodium sulfite. The use of sodium bisulfite for boiling-out cotton, however, does not seem to have come into very general practice, and therefore it may be presumed that it does not furnish satisfactory results.

Various other additions have been suggested in the matter of boiling-out compounds. For instance, it has been recommended to use a small amount of an oxidizing agent such as potassium bichromate, permanganate or perborate, especially in the case of boiling-out goods that contain colored stripes or patterns of vat dyes or indigo. This has been suggested for the purpose of preventing the reducing action of the kier liquor from destroying the color. Generally speaking, however, none of these processes have met with any degree of practical success, either from the fact that the energetic oxidizing action of the substances used caused a deterioration in the strength of the fiber, or by reason of the high cost of the process. Peroxides, however, have been used in connection with alkalies in the kier boiling of cotton with a certain degree of success, especially where it is desired to obtain a partially bleached material by one operation in the kier. This process is used to quite some extent in the simultaneous bleaching and dyeing of cotton knit-goods for the production of certain light shades of mock Egyptian, light blue, etc. The dyes of

course that are required must withstand the action of the peroxide and alkali boil. This method is much practised in America and is known as the "Autogyp" process.

14. Use of Steeping Process.

A feature of the boiling-out process which is not considered as much as it was formerly is the preliminary steeping of the goods in hot water previous to the kier boiling. This was nearly always done in former days before the advent of the pressure kier, and it seemed to be particularly necessary in the bleaching of linen. The steeping process had its good points in that it helped very materially to remove the impurities from the goods. It is highly probable that there was a distinct fermenting action taking place in the steeping process, and this rendered the starchy and pectin matters much more soluble than would have been the case if the goods had not been steeped. At the present time the steeping operation is still practised to some extent in the bleaching of linens, but with cotton goods it is seldom if ever used as a previous operation to boiling-out. It is probably too costly in expenditure of time and labor for the benefit obtained over the ordinary method now in use.

Steeping of cloth is really to be considered as a preliminary process to boiling-out. It is not so much practised at the present time as formerly, owing perhaps to improvements in the construction and operation of kiers which have lessened the importance and value of this process. It is said, however, that steeping is of more importance in the caustic soda boiling than when lime is used. The chief object attained in steeping is probably the softening and opening up of the fiber so that it may become more readily impregnated with the kier liquor. It is also a considerable aid in the disintegration and removal of the starchy sizing materials and even some of the pectin materials on the fiber. This is especially the case when the steeping operation is so conducted as to permit of a fermentation being engendered, and this is readily brought about by steeping the cotton in warm water for some hours. The most favorable temperature in this case is about 140° F., and care must be had not to allow the fermentation to become too active as otherwise the fiber itself may be attacked by the micro-organisms. The water employed for steeping should also be carefully looked into as the use of water containing moulds and putrefying bacteria may result in the growth of mouldy spots on the cotton which are subsequently very difficult to remove. The steeping operation as modified by the use of infusions of malt extracts is considered elsewhere as a separate process. Sometimes the steeping is conducted in acid liquors with the idea that the dilute acid will effect a partial hydrolysis of the starch and sizing materials and is also of aid in the dissolving and removal of miscellaneous dirt, so that the general impurities on the fiber are loosened up and thus are more easily removed in the kier boiling. The use of acid steeping liquors, however, in this connection is rather a dangerous procedure, owing to the difficulty of avoiding acid spots leading to tendering of the cotton. It

is also doubtful if steeping in cold and very dilute solutions of acid has the effect of hydrolyzing or solubilizing much of the starch in the size, and the use of hot liquors of this character would be accompanied by considerable danger to the goods. In the use of acid steeping liquors it is also necessary to keep the goods well submerged beneath the surface of the liquor, as otherwise local drying will occur with the formation of acid spots, which will afterwards show up as tender and discolored places.

The use of an acid steeping liquor is utilized in the Thies-Herzig process, for according to Georgevics,[9] in this process the goods are

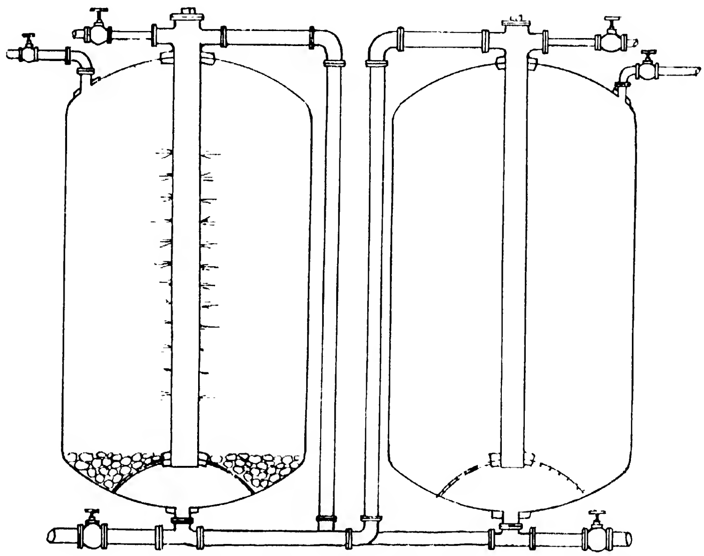

Fig. 124.—Diagram of Barlow Twin Kiers.

first steeped in a sour containing 1 percent of sulfuric acid (oil of vitriol, 60 percent) together with 0.005 percent of hydrofluoric acid (75 percent). The reaction may be accelerated by steaming the goods for 30 seconds before washing. After washing, the cloth is steeped overnight in a 0.5 percent solution of soda ash, and after this they are soaked in a 0.0005 percent solution of magnesium chloride, wrung out and then passed into the kier where they are boiled with a 7 percent solution of caustic soda. This preparation for boiling-out seems rather complicated and time-consuming and it is doubtful if it accomplishes results which are at all commensurate with the expense. The use of the magnesium chloride is said to allow of boiling with more concentrated alkali than otherwise, but as the magnesium salt acts

[9] *Chemical Technology of Textile Fibers*, p. 69.

in this manner simply because it neutralizes some of the caustic soda, the argument for its use does not seem to be sound.

15. Packing of Kier.

Careful packing of the goods (whether skeins, warps or cloth) in the kier for boiling-out is very essential to the production of satisfactory results. Special care should be taken to avoid the occurrence of vacant or loosely packed spaces where steam or air could accumulate. Also it is needless to say that the packing should be carried out in such a manner as to give as homogeneous a mass as possible so that the liquor will not tend to form channels when circulated. It is hardly possible to give a written description of a method for properly packing a kier, as the exact details will depend so much on the kind and character of the goods and the construction and form of the kier. This technique can only be acquired by considerable practice and careful observation. The use of mechanical coilers is only useful as an adjunct to hand operation, as it is only with the latter coupled with personal skill that a kier can be properly packed. It is usually considered best to saturate the goods with the kier liquor before they are packed in the kier, as then the kier boiling can be started up with much more ease than when the dry goods are used. In the case of skein yarn, of course, it will hardly be possible to first impregnate the material, but with warps and cloth it is comparatively easy to give a suitable saturation previous to running into the kier. Generally all that is necessary is to run the fabric through a box containing the caustic soda or milk of lime liquor and then through squeeze rolls and thence to the kier.

16. Bleaching Without Boiling-out.

There are isolated methods of bleaching generally known as "cold bleaching" where a boiling-out process is dispensed with entirely and the bleaching results are obtained by the use of hypochlorites in connection generally with soap liquors. While such methods may have found some use in a small way in particular instances of bleaching, apparently they have never been adopted in a large way for mill bleaching, and are only of interest in indicating that cotton may be bleached even rather satisfactorily without the use of a boiling-out operation.

While numerous recipes have been given from time to time for the preparation of the boil-out liquors for the kier, it is not well to recommend any one for general use. The particular kind of goods being treated, the method of operating, and the kind and construction and size of the kier to be used are all factors in determining the exact nature of the mixture or alkalies to use. These problems will be more completely discussed under the different processes of boiling-out. A large number of patents have been taken out for various compositions relating to the boiling-out of cotton, and while many of these are interesting, it is seldom that any of them are of any practical use. The bleacher himself usually develops a composition of his own to

meet the special requirements of the various conditions under which he operates.

There have also been attempts made to recover the alkali from spent boil-out liquors, but these have never met with any practical success owing to the fact that these liquors are quite dilute and are contaminated with such a large quantity of organic impurity, fats, waxes, starchy products and miscellaneous ingredients. During the process of boiling-out a great deal of the alkali is used up and it apparently does not pay to recover the rest as is the case with the cooking liquors from the soda pulp process in paper making.

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In the question of kier-boiling with lime these remarks are particularly pertinent, as early methods of boiling-out often called for certain details which, once considered very essential, were subsequently found to be useless complications and encumbrances.

It is probably impossible to determine at this time just when lime was first introduced for the kier-boiling of cotton; it was introduced evidently in the first years of the last century, for we have records at that time (1805) showing that its use for this purpose was forbidden

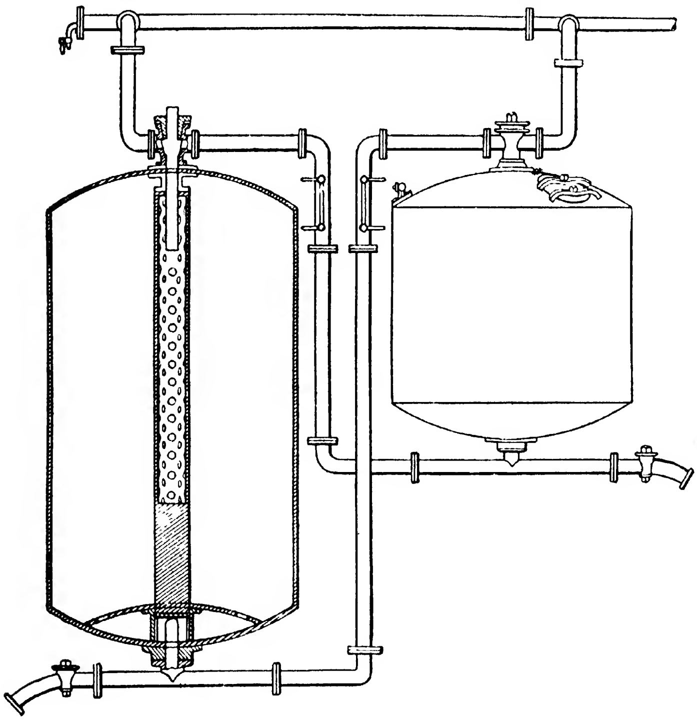

FIG. 125.—Pendelbury Kier.

by law as detrimental to good bleaching. Parkes (1815), however, mentions the use of milk of lime in England as the widely accepted method of boiling-out, so evidently the lime boil came into use rather quickly.

Lime, however, was apparently used at a very early date in connection with bleaching, for the Greek writer Xenophon (about 370 B. C.) tells of a ship loaded with linen fabrics and lime for their bleaching being wrecked near Marseilles, because a leak was struck in the bunker containing the lime. In the Middle Ages, however, the

rules of the bleaching trade guilds forbade the use of lime for fear of injuring the cloth.

The idea of employing the soda boil after the lime boil was introduced by an American, Mr. Dana, of the print mills of Prince and Dana, of Lowell, Mass. This led Albert Scheurer, of Mulhausen, to study the subject carefully and modify and greatly simplify the method of kier-boiling with lime. Scheurer's developments may be shown as follows:[4]

1835	1837
1. Steeping in water	1. Lime boil
2. Lime boil	2. Sour with hydrochloric acid
3. First caustic soda boil	3. First soda ash boil
4. Second caustic soda boil	4. Second soda ash boil
5. Ageing, chloring, souring	5. Souring
6. Third caustic boil	6. Chloring
7. Ageing and chloring	7. Souring
8. Fourth caustic boil	8. Washing
9. Chloring and souring	
10. Washing	

It may be seen from this that under the influence of Dana's discovery Scheurer greatly simplified the bleaching process in Europe, and prepared the way for a much greater simplification later on in the boiling-out process. In the Dana process itself there was no sour with hydrochloric acid between the lime boil and the soda boil; this idea was introduced apparently by Scheurer and was a distinct improvement. Moreover Scheurer was perhaps the first to bring a thorough chemical knowledge to bear on the subject and to furnish a clear explanation of the probable action of the lime, the soda ash and the reason for introducing a sour after the lime boil. It is not to be understood from these remarks, however, that Scheurer was the first to introduce souring (treatment with dilute acid solutions) as a process in the treatment of cotton previous to bleaching. This was quite an old operation, and can be traced back to the use of sour milk (which contains lactic acid) as a means of whitening fabrics, and later on other acids were employed, including acetic, sulfuric and hydrochloric; but these were all employed as adjuncts to the grass method of bleaching, and Scheurer was the first to introduce it in connection with the boiling-out process. Home[5] in the latter part of the eighteenth century in fact mentions the substitution of sulfuric acid for sour milk in the bleaching of fabrics.

Scheurer selected hydrochloric acid in place of sulfuric as he knew that the chloride of calcium was much more soluble than the sulfate, and hence should be more easily removed from the goods. But even this fact was recognized by Kurrer in 1831.[6]

2. Early Studies of Boiling-out Processes.

Attention has already been drawn to the fact that real progress in the development of the boiling-out process was not possible until

[4] Theis, *Die Strangbleiche*, p. 42.
[5] *Essai sur le blanchiment des Toiles*, Paris, 1762
[6] *Die Kunst vegetabilische Stoffe zu Bleichen*, p. 24.

the introduction of chemical science allowed of a clear understanding of the nature of the impurities on the fibers and of the action of the various chemicals available on these, and also on the fiber itself. In a French book published in the eighteenth century by D'Apligny on *The Art of Dyeing Cotton*, and translated into English in 1789, there is a passage on the bleaching of vegetable fibers which is entertaining, if

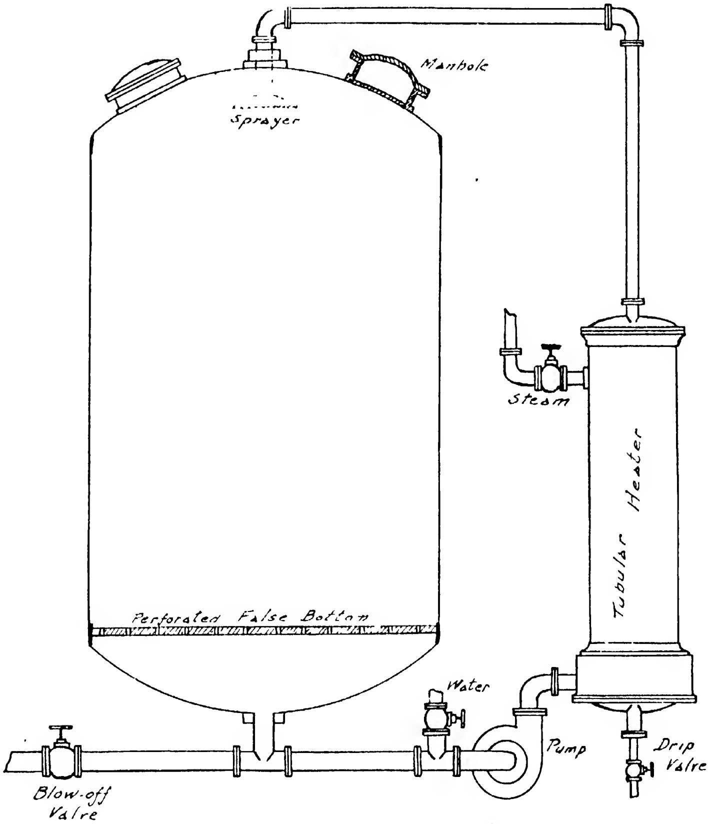

FIG. 126—Diagram of Walsh Kier.

not instructive. D'Apligny writes as follows: "The process of bleaching is nearly the same in all countries; it differs only in the time and mode of operation. This difference is not to be wondered at, since it is founded on the nature of the material to be expelled in whitening. Flax, hemp, and all other vegetable substances capable of producing thread are impregnated with a considerable quantity of sweet oil, not volatile, mixed with the mucilage of the plant. Fixed alkalies combined with the oily particles, form together a soap, the solution of

which in water would be prevented by the mucilage forming a mastic with the oil; now this mastic can only be detached from the thread by exposing it to the heat of the sun, by which this alkali is volatilized. But the thread, though washed and several times dried, is not yet sufficiently whitened. I have already said that one portion of the mucilage which forms the epidermis of the stalks, having been baked by the heat of the sun, is so extremely hard that lixiviums cannot touch it. Besides, the soapy matter which can neither be volatilized nor carried off by alternately watering and drying the thread, must by the volatilization of the alkali be transformed into an absorbent earth. Many bleachers use lime, and by frequently sprinkling and exposing to the sun, load the thread with this substance; it is therefore necessary to carry it off, which cannot be effected by washing the thread, because the earth will not dissolve in water. Acids only are capable of destroying it, which with the absorbent earth compose a neutral salt, soluble in water, and consequently may be removed by washing the thread well. The acids commonly used are sour milk, or an infusion of bran or flour of rye kept till it becomes sour. Some imagine that the sour whey makes the thread yellow, caused by the oleaginous particles of the milk, and therefore prefer the juice of sorrel. Those who understand their own interest have recourse to the oil of vitriol; this, though diluted in a great quantity of water, has the property of completing the whitening of the thread. In this state it cannot possibly injure the thread in any respect; it detaches the chaffy particles still adhering to the thread for want of sufficient maceration, and also the earth."

Perhaps the first systematic investigation or study of the subject of bleaching was by the Scottish physician, Francis Home.[7] He apparently made definite experiments as early as 1750 on the use of the then known alkalies in the boiling of cotton and linen previous to bleaching. He came to the conclusion that the use of soda ash in boiling should be avoided and in its place there should be used potash caustified with one-fourth of its weight of lime. Home also recommended the use of dilute sulfuric acid as a sour treatment after boiling-out in place of the treatment with bran water or sour milk. Home's experiments had chiefly to do with the treatment of linen, as cotton at that time was little used in its bleached form. A little later, however, Gülich[8] published considerable matter relating to the bleaching and treatment of cotton which contains much of interest. A brief résumé of the process then used to serve as a comparison with the methods now in vogue may be of value to our readers. Gülich states that first a caustic lime liquor is prepared by mixing clear lime water and potash together, using ¼ pound of lime and ¼ pound of potash for the treatment of each pound of cotton. The cotton yarn or cloth is then steeped in this lye for 6 to 12 hours, being worked therein with the hands or feet to obtain satisfactory impregnation. After this preliminary steeping process the goods were given a real boiling in a potash

[7] *Essai sur le blanchiment des Toiles*, Paris, 1762.
[8] *Vollständiges Färbe und Blaichbuch*, Ulm, 1780.

lye and then soured in oil of vitriol and exposed to the sun. These operations were repeated a number of times until the desired degree of whiteness was obtained. Gülich goes into great detail concerning the various steps of the process, particularly with reference to the preparation of the lye solutions.[9]

This will give the reader some idea of the rather peculiar notions then prevailing concerning the purification of cotton. With the introduction of kier-boiling a far better conception of the process was introduced, and since the introduction of exact chemical investigation much further progress has been made. It may still be said, however, that there is a great field for the chemist in this industry. Hardly any two bleacheries even at the present time adopt exactly the same method of procedure in boiling-out; there is still argument over the question of whether the lime boil or the caustic soda boil is the better; some claim even yet that the lime boil will give a bleached white which will stand storing better than the caustic soda boil and will not turn yellow with age; others claim that the opposite is true. All through the general process of both boiling-out and bleaching there are points of dispute as to whether this method or that method is right. There is only one sensible method of settling all of these matters, and that is by the systematic investigation of all the various factors in the process in an unprejudiced manner, and collecting in this manner a series of data which may then be properly collated and compared in order to arrive at the standardization of the process. Opinions of one bleacher as against another are generally useless and misleading; nearly every bleacher has his pet notions concerning the proper conditions of boiling-out, and he is usually so wedded to these that it is hard to convince him that some little point which he may consider of great importance in the ultimate success of his work is really a negligible factor, and he turns out an excellent bleach not on account of this mysterious factor, but frequently in spite of it.

3. The Lime Boil.

The first distinct advance in the bleaching of cotton was in the development of the lime boil and the more or less standardization of that process by means of chemical study and control. Though this method is of far less importance at the present time than it was formerly, still it must be studied with considerable care and detail in order to make one generally familiar with the subject of bleaching.

The method of boiling-out cotton with lime involves several operations, as follows:

(a) Boiling with milk of lime in a closed kier
(b) Souring with dilute sulfuric acid to remove lime compounds. This operation is known as the gray-sour
(c) Boiling with soda ash or caustic soda with or without the addition of resin soap

[9] Other writers of interest on the matter of boiling-out cotton or linen before bleaching are Erxleben, *Die bohmische Leinwandbleiche*, Vienna, 1812, and Higgins, *Versuch über die Theorie und Praxis des Bleichens*, Halle, 1802.

At the present time lime boiling is confined exclusively to the treatment of cotton cloth, and even in this field its use is becoming more and more limited as it is gradually being replaced by the caustic soda boil.

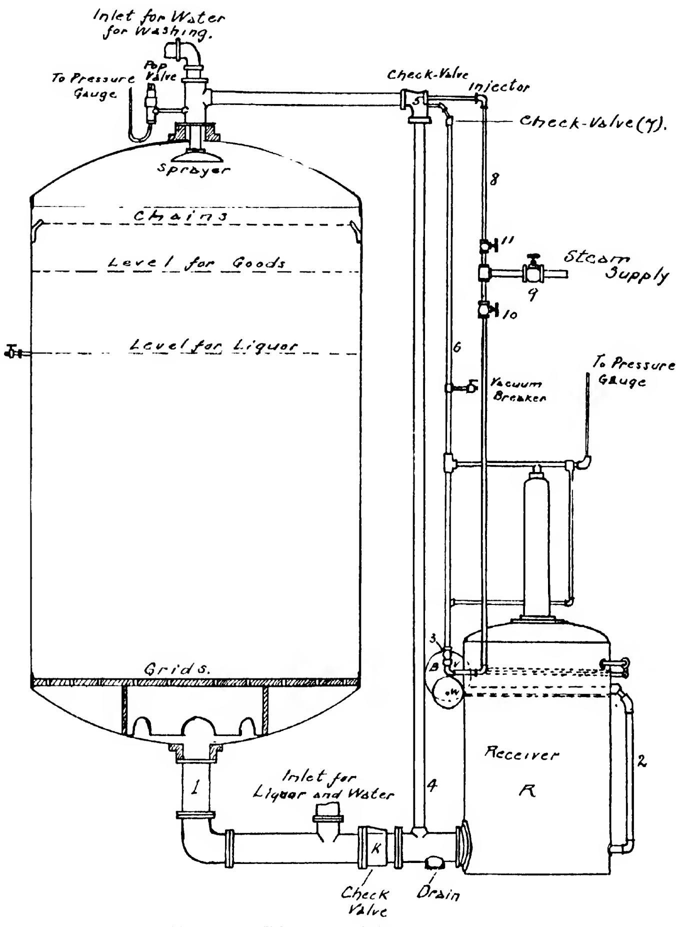

FIG. 127.—Diagram of Jefferson Kier.

It has been claimed in favor of the lime boil that the presence of the lime protects the fiber from mercerization. Trotman and Thorp, however, point out that this can hardly be tenable, since, if the souring process is properly carried out, there will be no lime present in the subsequent alkali boil; and further, any calcium sulfate or chloride left would be converted into calcium carbonate by the soda ash in

the alkali boil. When the goods are impregnated with calcium or magnesium chloride solutions, as in the Thies-Herzig process, strong solutions of caustic soda may be used without danger of mercerization, but in this case there is actually present calcium or magnesium hydrate owing to the reaction of the salts with caustic soda.

It is sometimes claimed that the lime boil is less expensive and gives a better "bottoming" for bleaching than the caustic soda boil, but apparently neither of these contentions can be substantiated with accurate figures or evidence which will bear the scrutiny of scientific investigation. That a properly conducted soda boil will give a preparation or bottom to cotton which is in every respect complete and satisfactory, we believe has been established beyond any question. From analyses made on cloth boiled with lime and with caustic soda it would appear that in the latter case the removal of fatty matters and nitrogenous compounds was even more complete than with lime. This has been confirmed by experiments made by Trotman and Thorp[10] even when using hydrochloric acid as the sour for decomposing the lime soaps. When sulfuric acid was used the lime left in the fabric was quite considerable, amounting in some cases to as much as 0.52 percent, and consisting partly of lime soap and partly of carbonate and sulfate of lime. The following shows the results of these tests:

Constituents	Caustic Soda Boil Percent	Lime Boil Percent
Ash	0.26	0.52
Free fat	0.10	0.26
Fatty acids as soap	0.16	0.22
Nitrogen	0.05	0.70

The claim that heavy weight fabrics are better boiled-out with lime than with caustic soda would seem to be rather anomalous as the penetration of the caustic soda liquor would be more rapid and thorough than the lime solution. Furthermore, the question of cost is usually argued simply from the point of view of the relative value of the chemicals employed, without taking into consideration the greater time required, the greater amount of steam and water, and the greater complexity of the process in the case of the lime boil necessitating more handling of the goods and a greater labor charge. It may be said that in the boiling-out of all goods that are in a dense package form, such as beamed warps, cops, tubes, cheeses, compressed loose cotton and sliver, it is always necessary to use a caustic soda boil as the lime liquor will not give a satisfactory penetration or impregnation.

4. Character of Lime Used.

For the lime boil a good quality of fat lime should be selected. By fat lime is meant one which contains but a small proportion of magnesia and silica, and slakes readily. Care should be taken also that the lime has not been exposed too long in the air, as this will convert a considerable part of it back into the carbonate. In preparing the milk of

[10] *Bleaching and Finishing of Cotton Goods*, p. 95.

lime for use, the lime should be slaked and then diffused through water, for which purpose a sheet-iron tank may be used, and the lime should be contained in a cage-like sieve in order to prevent large lumps

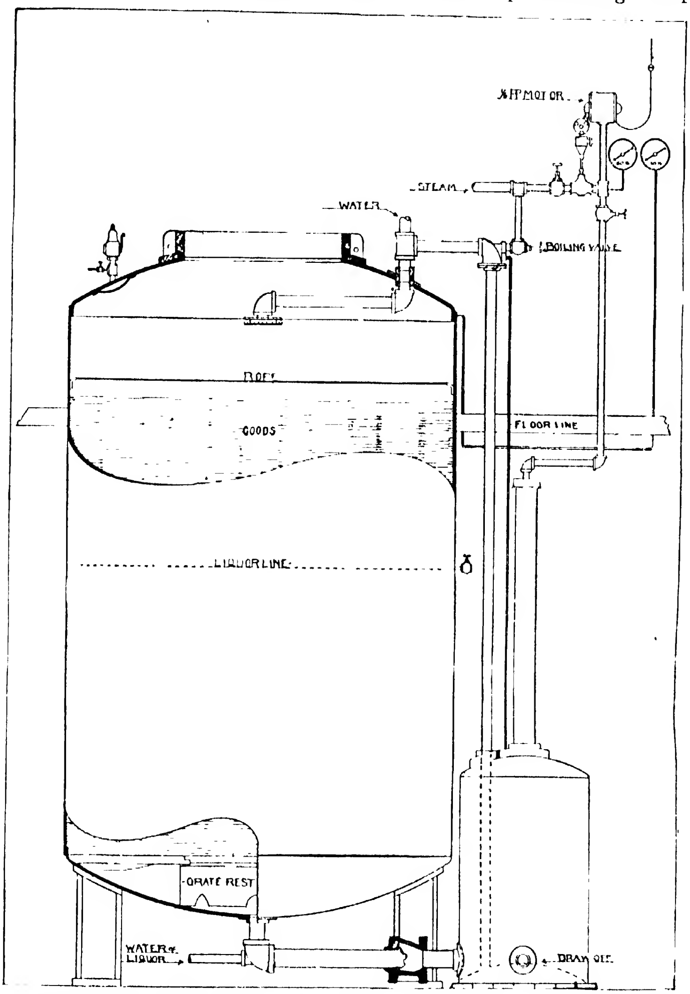

FIG. 128.—Jefferson Kier with Time Valve and Electric Control Circulator.

from entering the liquid. The lime should be well stirred into a paste in order to insure that there are left no unslaked particles which might otherwise "burn" the cotton on coming in contact with it. Lime that has any considerable amount of iron in it should not be employed for

boiling-out as stains are very liable to result. The following table shows the density of milk of lime of various strengths:

Degree Bé.	Density	CaO in 100 lbs.	CaO in 10 gals.
10	1.074	10.6	13.3
12	1.091	11.6	15.2
14	1.107	12.7	17.0
16	1.125	13.7	18.9
18	1.142	14.7	20.7
20	1.161	15.7	22.4
22	1.180	16.5	24.0
24	1.199	17.2	25 3
26	1.220	17.8	26.0
28	1.241	18.3	27.0
30	1.262	18.7	27.7

In preparing the lime solution, or rather the milk of lime, usually a sheet-iron tank is used provided with a suitable arrangement for diffusing the lime through the water.

At the present time a form of slaked lime known as "chemical lime" is quite extensively used, and this can be made up into a milk of lime liquor directly by simply mixing with water, and in this way the disagreeable features of slaking large lumps of quicklime are avoided; also the use of this powdered chemical lime does away with the danger of small particles of unslaked lime getting into the liquor. This is a feature which is often a source of trouble as it may give rise to defects in the cloth, as already pointed out. Chemical lime, however, is somewhat more expensive than lump quicklime, and this must be taken into consideration in calculating the proper economies of the process.

The milk of lime liquor is nearly always introduced into the goods by passing the fabric through a box or cistern containing the lime liquor of suitable strength and then through light squeeze rolls and into the kier. In this way the goods become more or less evenly saturated with the lime as they pass into the kier, and this helps to promote an even distribution of the lime and a uniformity of action in the kier-boiling. The strength of the lime liquor should be so maintained that practically all of the lime is thus fed onto the goods when the kier becomes completely loaded.

5. Details of Lime Boiling.

The quantity of lime required will naturally vary with different classes of goods; but in general it will be from 3 to 12 percent of the weight of the cloth. When the cloth is first saturated in milk of lime outside of the kier, the liquor should be of such a consistency that the material takes up about 5 percent of its weight of lime. The time of boiling will vary from 8 to 10 hours with the character of the goods and the pressure employed. After boiling, the lime-water must be quickly run off and the kier filled with cold water as rapidly as possible, in order to prevent the lime drying on portions of the goods coming in contact with the hot walls of the kier, as this will cause uneven

streaks and spots to appear afterwards. Kiers employed for lime boiling are usually white-washed from time to time on the inside in order to prevent rust from forming and thus contaminating the goods.

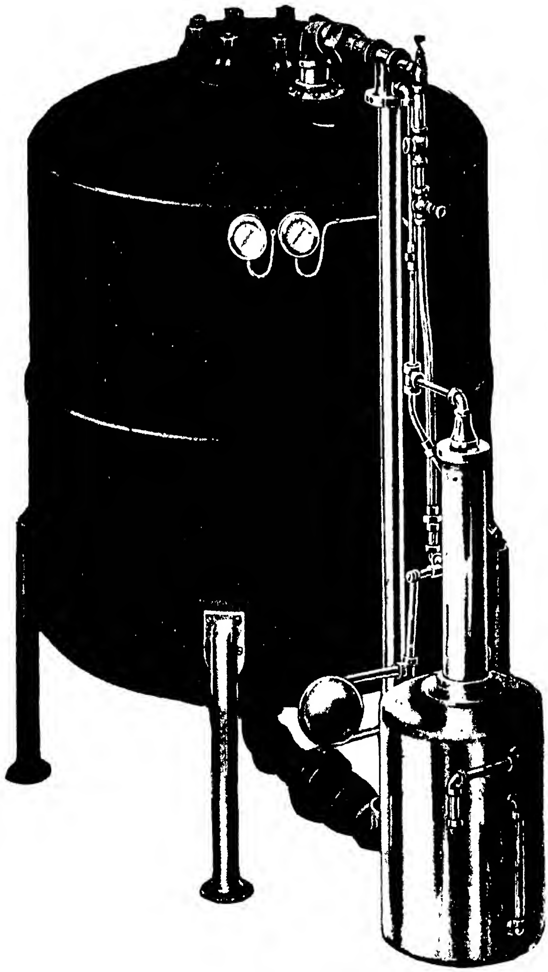

FIG. 129.—Jefferson Kier showing Exterior View.

After being removed from the kier, the goods are washed in a machine, and then passed on to the next operation of souring.

The principal effect obtained by boiling in milk of lime is to de-

compose the fatty and greasy matters present in the cloth. These substances are not to be considered as removed from the fiber, as the insoluble lime soaps which are formed still adhere to the cloth, but they are removed in the subsequent processes. The color of the cotton after the lime boil is usually darker than before, and this is especially the case with goods made from Egyptian cotton.

6. Use of Strontia.

Since strontia (strontium oxide, SrO) and baryta (barium oxide, BaO) are alkaline earths of a character very similar to that of lime, it would be natural to expect that they might act in kier-boiling in a manner very similar to lime. Weiss [11] has made an interesting comparison of the action of these three alkaline earths in the boiling-out of cotton containing oil stains. The saponifying power of baryta was found to be inferior to that of lime, but strontia, in equi-molecular proportions, was found to saponify the oil three times more rapidly than lime, and the bleaching effects were superior. The maximum concentration of the boil-off liquor was fixed at 20 grams of strontium hydrate ($Sr(OH)_2.8H_2O$) per liter, as stronger solutions were found to have an oxidizing action. Strontia also absorbs carbon dioxide more rapidly from the air than lime. It is proposed to run the goods through a solution of strontia, pack the cloth down in cages, boil 8 to 9 hours in the kier, rinse, sour by transferring the cages to the souring vat, reboil in the old kier liquor, sour again, give a slight boil in a caustic soda-soda ash liquor with the addition of a little soap, sour and wash. A fairly good color is said to be obtained in this manner without the use of hypochlorite liquors. A better boil-out is obtained by using a mixed liquor containing 7 grams of caustic soda and 10 to 12 grams of strontium hydrate per liter. The goods are boiled for 2 hours at a temperature below 150° C., soured, rinsed, and reboiled in a liquor containing soda ash, soap and resin at a moderate temperature to avoid yellowing. The strontia process of boiling-out, however, does not seem to have attained any commercial success owing to the higher cost of the strontia and the danger of tendering the goods.

7. Importance of Circulation.

In kier-boiling too much importance cannot be attached to the proper circulation of the liquor through the goods. It has been well demonstrated that the time required for a complete boiling-out is much reduced by rapid and efficient circulation. If the circulation is not good, but allows the same liquor to remain for some time in contact with the goods, such liquor becomes weakened in its effective properties. A proper circulation should so operate as to be continually bringing fresh liquor in contact with the material. Most modern kiers are provided with an automatic arrangement for the promotion of a constant and proper degree of circulation. The old-fashioned kiers mostly relied on the action of a steam injector both to promote the circulation of the liquor and to heat it, but in such a system the intro-

[11] *Bull. Soc. Ind. Mul.*, 1914, p. 499.

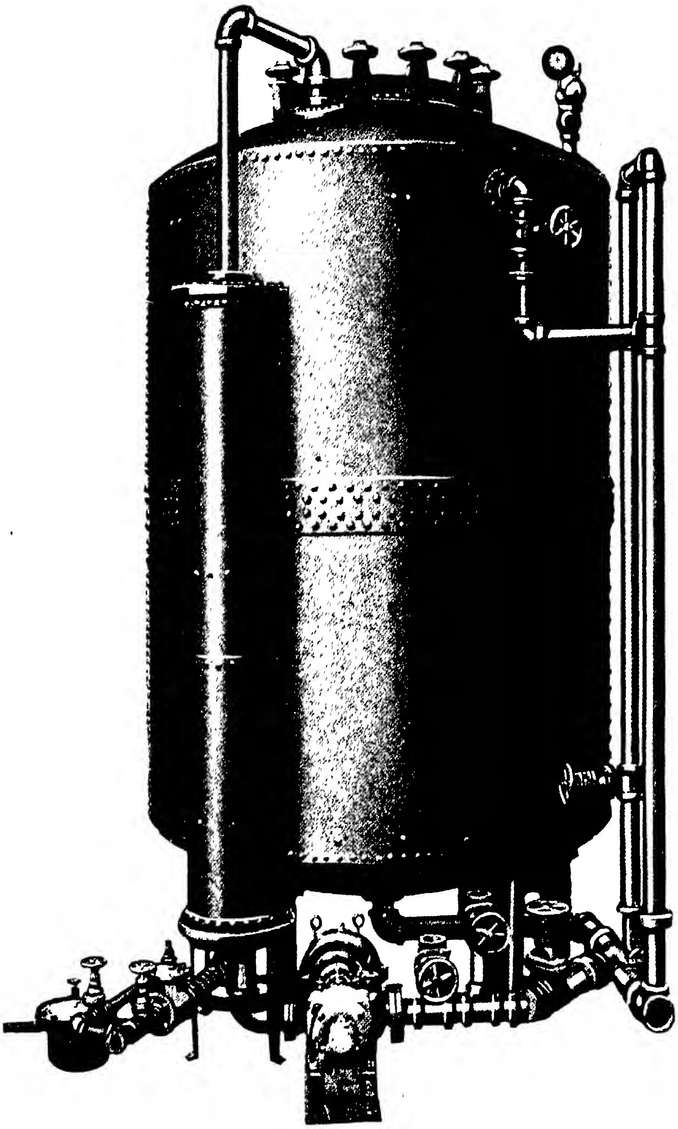

FIG. 130.—Allen-Worcester Kier with Electric Driven Circulator and Outside Heater.

duction of the steam must be intermittent, as otherwise the liquor would soon acquire the same temperature as the steam, with the result that steam or foam alone would blow over through the kier without causing any circulation of the liquor. In more recent times the tendency in kier construction seems to favor the use of an outside means of circulation, either as a pump or a vacuum chest. The mat-

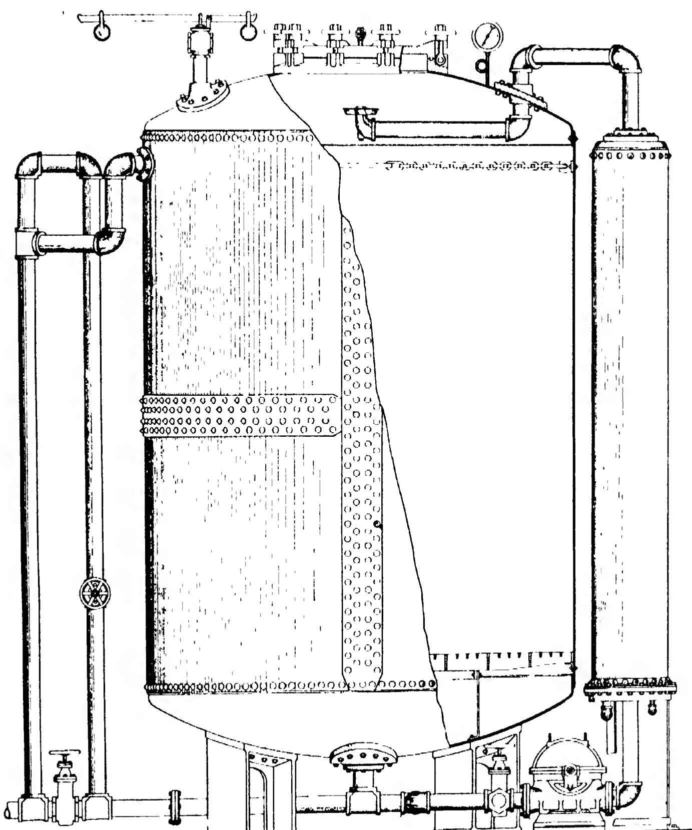

Fig. 131.—Diagram Showing Construction of Allen-Worcester Kier.

ter of kier circulation, however, and the methods of producing it will be dealt with in more detail under the consideration of the kiers themselves.

8. The Gray Sour.

In some processes of bleaching the cloth is not boiled-out first with lime but with caustic soda and afterwards with lime; but whenever the lime method is used, it is necessary to follow it by a treatment

with dilute acid in order to remove the lime compounds from the cloth. This operation is known as the lime sour or gray sour, and consists in passing the goods through a solution of sulfuric or hydrochloric acid at about 10° Tw. The machine employed is generally the usual form of roller washing machine. In the gray sour hydrochloric acid is to be preferred to sulfuric as the latter forms an insoluble compound with lime, while the former does not, and hence the lime soaps are the more easily removed. The acid bath is usually employed cold, but by using warm solutions, the strength of the acid may be considerably diminished with the same effects as far as cleansing is concerned, and also there will be a saving in time. After the souring process is completed the goods should be well washed, for they should not be left for any length of time with the acid liquor in them as tender spots are liable to develop. The effect of the gray sour is to decompose and remove the various lime compounds left in goods from the previous operation, together with any metallic oxides that may be in the fiber.

9. Boiling with Soda Ash.

After the lime sour the next step is to boil the goods with soda ash in kiers similar to the ones used for the lime boil. It may be observed that soda ash must not be used in the same tanks or kiers as employed for the lime boil, as the lime present would change the soda ash into caustic soda and so alter the strength of the lye; also the soda ash would precipitate the lime as carbonate. In some bleacheries there are two boils made in soda ash, while in others there is only one; also the strength and character of the liquors will vary much with the character of the goods and the methods of operation, so it is almost impossible to lay down any set rules for this process. Some observations, however, will be of service. When open or low pressure kiers are used, the duration of boiling is generally from 8 to 12 hours, while with an injector kier and several atmospheres pressure, the time of boiling may be reduced to 3 to 4 hours. The goods must be packed systematically into the kier in the same manner as described in lime boiling, and the cloth may either be saturated with the lye before entering the kier, or the lye may be run in afterwards. By saturating before, the goods will pack better and there will be less air in the folds.

10. Use of Resin Soap.

Formerly boiling in resin soap was largely employed, especially for goods intended for print cloth, as it was supposed that the resin removed certain matters in the fiber which attracted coloring matters, and consequently gave clearer whites to the printed calico. The boiling with resin soap, however, is not used as much as formerly, but if it is employed, it is given in the first lye boil. About 1 to 2 percent of rosin (of the weight of the goods) is dissolved in 5 to 6 percent of soda ash and the goods are boiled in this mixture for several hours under pressure.

When resin soaps are used in boiling-out, according to Trotman and

duction of the steam must be intermittent, as otherwise the liquor would soon acquire the same temperature as the steam, with the result that steam or foam alone would blow over through the kier without causing any circulation of the liquor. In more recent times the tendency in kier construction seems to favor the use of an outside means of circulation, either as a pump or a vacuum chest. The mat-

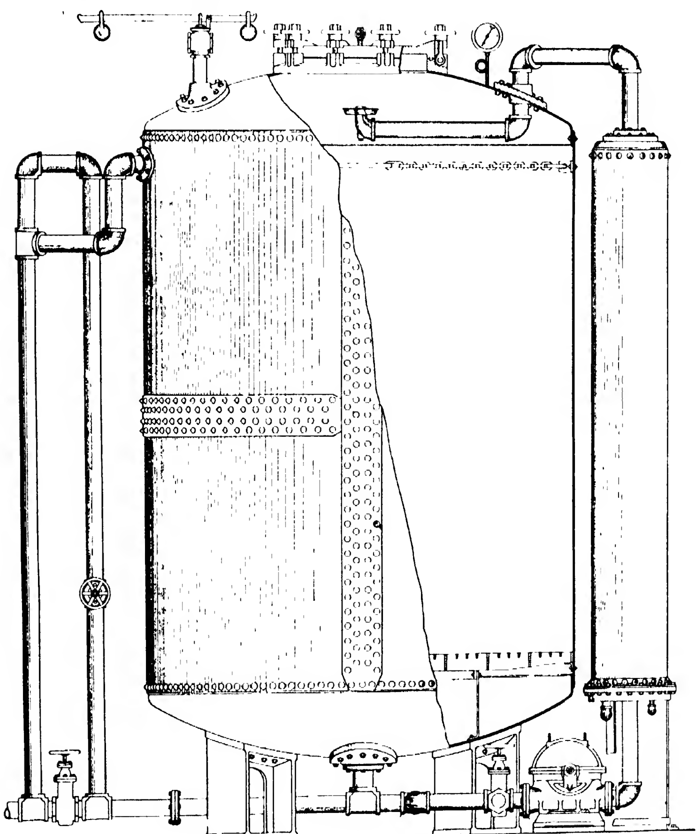

FIG. 131.—Diagram Showing Construction of Allen-Worcester Kier.

ter of kier circulation, however, and the methods of producing it will be dealt with in more detail under the consideration of the kiers themselves.

8. The Gray Sour.

In some processes of bleaching the cloth is not boiled-out first with lime but with caustic soda and afterwards with lime; but whenever the lime method is used, it is necessary to follow it by a treatment

ash, the goods must again be washed in order to remove the excess of alkaline liquor and the dissolved impurities. The coloring matters, however, of the fiber have not yet been attacked, and the cloth is still in the gray condition, and usually darker in color than before boiling-out.

The following table represents the number of pounds of different alkalies to be taken per 100 gallons (U. S.) of solution in order to furnish a lye of certain strength:

Degrees Bé.	Lbs. Soda Ash	Lbs Caustic Soda
0	0	0
0.5	2¾	2½
1.	5¾	5
1.5	8½	7½
2.	11¼	10
2.5	14	13½
3.	16½	17

11. Hygrometric Scales.

As different bleachers may make use of different scales of hydrometers, the following table is given showing the relation between the different systems:

Sp. Gr	Bé	Tw.	Beck	Sp. Gr.	Bé	Tw.	Beck
1.	0	0	0	1.134	17	26.8	
1.007	1	1.4		1.143	18	26.6	
1.014	2	2.8		1.150	19	30.	23
1.022	3	4.4		1.161	20	31.2	
1.029	4	5.8		1.171	21	34.2	
1.036	5	7.2		1.180	22	36.	
1.044	6	8.8		1.190	23	38.	
1.050	7	10.	8	1.199	24	40.	29
1.060	8	12.		1.210	25	42.	
1.067	9	13.4		1.250	30	50.	34
1.075	10	15.		1.300	34	60.	40
1.083	11	16.6		1.350	38	70.	44
1.091	12	18.2		1.400	41	80.	49
1.100	13	20.	16	1.450	45	90.	53
1.108	14	21.6		1.500	48	100.	57
1.116	15	23.2		1.530	50	106.	59
1.125	16	25.					

Although weight for weight, fabrics will occupy different volumes according to their nature, yet it has been found in general that 100 pounds of cloth will require about 72 gallons of liquor. On this basis the following table is calculated showing the percentage of alkali on the weight of fabrics according to the density of the lye:

Degrees Bé.	Lbs. Per 100 Lbs. of Cloth Sodium Carbonate	Caustic Soda
0.5	2.4	2.
1.	4.8	4.
1.5	7.2	5.6
2.	9.6	7.2
2.5	12.	86
3.	14.	10.2

12. Composition of Spent Liquors.

Knecht and Hall[12] have made some studies on the composition of the extract from cotton with the different processes of boiling-out. An examination of the lime liquor obtained after boiling-out showed a gelatinous precipitate with alcohol, free from nitrogen and corresponding to pectic acid. The portion soluble in alcohol gave two brown resinous substances of different solubilities, containing 9.1 and 9.6

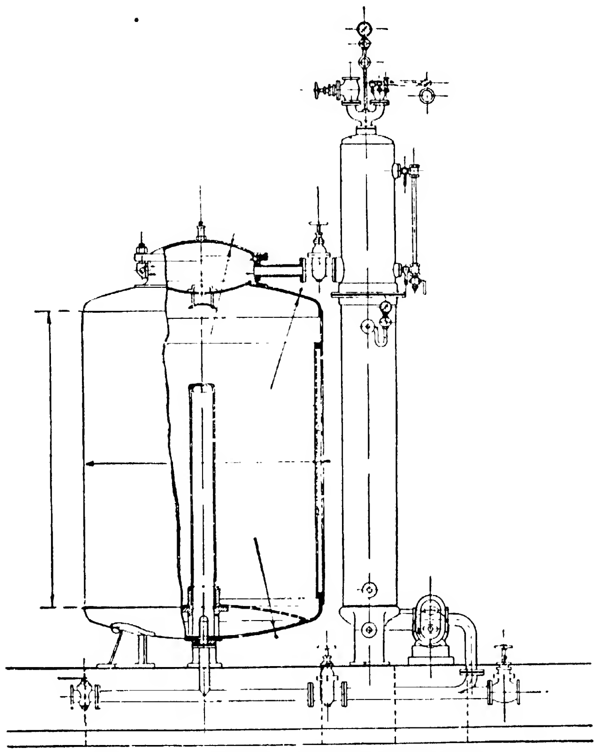

FIG. 133.—Diagram of Gebauer Section Kier.

percent of nitrogen respectively, and apparently consisting of coloring matters. There was also found a small quantity of fatty acid. The total extract from the cotton by the lime boil amounted to 2.1 percent, and this included the greater portion of the mineral constituents of the cotton. The lime sour (hydrochloric acid) showed extractive matters consisting mainly of a fatty acid corresponding apparently to stearic acid, together with a dark colored wax having a melting point of about 80° C., there also being a small quantity of a brown resinous

[12] *Jour. Soc. Dyers & Col.*, 1918, p. 220.

substance similar to that in the lime extract. The caustic soda extract yielded a brown residue fairly rich in nitrogen and phosphoric acid. On acidification of the soda extract, a dark colored protein containing 18.7 percent of nitrogen was precipitated. The total substance extracted from the cotton by these three main treatments was about 4 percent. It was also noticed that the hygroscopic moisture of the raw cotton was 7.36 percent while that of the scoured and bleached cotton was only 6.14 percent.

The composition of spent liquors is still a subject that is open to considerable investigation, and the chemist in this particular instance could be of much value to the bleacher, as a proper chemical analysis of the materials present in the spent liquor might throw considerable light on the entire subject of boiling-out. There is also a possibility of the discovery of valuable and useful by-products in the ingredients which may be present.

Chapter XIV.

The Boiling-out of Cotton *(Cont.)*.

1. The Caustic Soda Boil.

The rather complicated processes involved in the lime boil and the length of time required to carry it out has led bleachers to adopt simpler and shorter methods. By the use of caustic soda in boiling-out, the process may be reduced to one operation requiring only a few hours.

In the caustic soda boil the goods are boiled in either open or closed kiers with a solution of caustic soda. When open kiers are used the usual time required is from 8 to 12 hours; whereas when closed pressure kiers are used the time varies from 2 to 10 hours, depending on the character of the material and the thoroughness of the boil-out. Frequently in addition to caustic soda other alkalies are used, such as soda ash, sodium bicarbonate, soap and sodium silicate. The strength of the caustic soda lyes employed will vary considerably with conditions, but usually from 2 to 5 percent on the weight of the goods is used.

2. Loss in Boiling-out.

The loss in weight incurred by cotton in the process of boiling-out is an interesting factor in the consideration of bleaching. Dreaper states that on boiling cotton with a one percent caustic soda solution for one-half hour the loss in weight of the cotton was 4.41 percent; and after boiling for 1 hour the loss was 5.71 percent; while with the use of a 2½ percent caustic soda solution the losses were 5.08 and 7.3 percent respectively. Hunger, on the other hand, states that with a caustic soda solution of 10 percent strength and boiling for one-quarter hour the loss was only 4 percent, and when the concentration of the caustic soda solution was reduced to 2.5 percent the loss was 3.5 percent. The discrepancy must be due to some difference in the conditions of the two tests so that they are not comparable. Tauss has shown by other experiments that the solubility effect of the caustic soda solution in boiling-out increases with the pressure and temperature of the kier. At a temperature of 150° C. the loss in boiling-out for caustic soda lyes of 1 to 5 percent is 5 to 7 percent. Above 150° C. the loss increases rapidly showing evidence of decomposition of the cotton itself. Scheurer found that even on boiling cotton with plain water at temperatures about 150° C. a decided weakening of the material occurred. From the experiments of Schwalbe, it appears that

the most satisfactory strength for the caustic soda solution is 4 percent, as with weaker or with stronger alkalies the results are not as good. The amount of loss in boiling-out under practical mill conditions cannot be stated as a fixed figure owing to the fact that this loss varies considerably with the character of the goods being treated, whether loose cotton, yarn or cloth; and also with the kind of cotton, and the nature and amount of the sizing materials that may have been used in preparing the yarn for weaving. More important for the mill is the

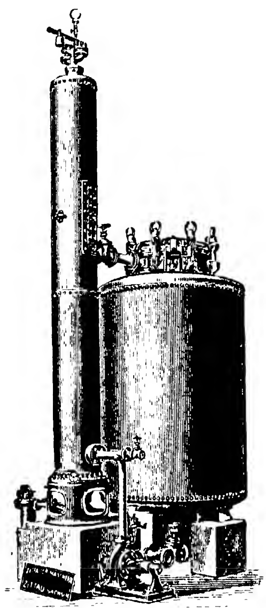

FIG. 134.--Sectional Kier of Gebauer Type with raised super-heater.

total loss in complete bleaching, and this includes the loss both in boiling-out and bleaching with hypochlorites and treatment with acids. It has been shown by Trotman [1] that the purity of the caustic soda liquor is of more importance than is generally supposed. Experiments were conducted in boiling-out with the use of pure caustic soda solutions as compared with caustic soda containing varying amounts of impurities, such as common salt, glauber salt and alumina, these being the principal impurities liable to occur in small amounts in commercial caustic sodas. The loss in weight of the cotton incurred during the boiling-out was taken as the measure of the efficiency of the boil-out liquor, and it was found that even very small amounts of these impuri-

[1] *Jour. Soc. Chem. Ind.*, 1910, p. 249.

ties reduced the action of the alkali very materially. With pure caustic soda, for example, the loss on boiling-out a certain quality of cotton was 4.47 percent; with a caustic soda containing 0.13 percent of common salt the loss was 4.08 percent, and with a caustic soda containing 0.30 percent of common salt the loss was only 3.98 percent. The influence of small amounts of glauber salt was in about the same proportion.

If kier-boiling has been properly conducted cotton yarn should have a greater breaking strength than in the raw state. This is especially true for cloth, where the shrinking and partial felting of fibers will produce an increased tensile strength. In fine goods, such as lace curtains, and in materials of a very flimsy and loosely woven character, it is possible that kier-boiling may cause some degree of weakening due to the mechanical strain to which the fine yarns may have been put in handling. Any very noticeable weakening, however, brought about by boiling-out in kiers will indicate a defect in the process, which may be either in the mechanical handling of the goods or in the chemical treatment to which they are subjected. Decrease in the tensile strength of goods after final bleaching is usually to be attributed to other operations than that of kier-boiling.

3. Shrinkage of Yarns.

In the boiling-out of cotton yarn a certain shrinkage in the length of the yarn will be experienced. This will be true of both skein and warped yarns as far as the kier-boiling is concerned; the same will also be true of cloth; but in both the warp and the woven fabrics the goods are handled in the rope form in the subsequent washing and bleaching operations, consequently owing to the considerable longitudinal tension under which the goods are placed, it will usually be found that the shrinkage caused in the kier-boiling will be more than compensated for, and consequently the goods will show a stretching rather than a shrinkage. With skein yarns, however, the average loss is length is about 2.5 percent. It is stated that in commercial operations it is usual to allow 5 percent loss on such yarn, but this must refer to the loss experienced as a final result of the entire bleaching operations rather than that due to kier-boiling alone.

4. Change in Count of Yarns.

As kier-boiling causes a loss in weight in cotton yarns as well as a loss in length, it will be apparent that the count or size of the yarn will show some change, as it depends on the relation of these two factors, weight and length. According to Trotman the count of the yarn is somewhat increased after boiling-out, which means that the yarn has become finer in size. This is accounted for by the fact that the loss in length is not sufficient to compensate the loss in the weight. It does not appear possible, however, to arive at a definite figure as to the alteration in count for yarns in general or to adopt an established factor, as this varies according to the size and the quality of the yarn, and probably is somewhat dependent on the conditions of manufacture and the nature of the cotton from which the yarn is made.

Cotton that has been boiled-out with caustic soda lyes will be darker in color than the raw cotton, and the spent lyes will have a brown color due to the impurities removed from the fiber. The loss in weight of the cotton boiled-out with caustic soda is about 5 percent. When boiled-out with other alkaline salts the loss in weight is not as much; and if this loss is accepted as a measure of the degree of boiling-out, it must be concluded that these other alkaline salts are less efficient agents than caustic soda alone. The use of caustic soda alone, however, especially in closed pressure kiers, is liable to make the cotton harsh to the feel, and on this account some bleachers prefer to use a mixture of caustic soda with either soda ash or sodium silicate. Such mixtures leave the boiled-out cotton in a softer condition, and with a much lighter color.

5. Treatment After Boiling-out.

After the boil-out with caustic soda has been completed, the liquor should be run off from the goods before cooling, as otherwise the cotton will take up considerable color from the cooling liquors, and there is liability of the formation of stains. To indicate whether any caustic soda remains in the liquor after a boiling operation, Higgins has found the following simple method very serviceable: If a mixture of caustic soda and soda ash has been used for the boiling, barium chloride is added to the hot exhaust lye and the liquor allowed to settle. The clear liquid is then titrated in the usual way for caustic soda. The precipitate of carbonate takes down with it most of the brown matter contained in the liquor, and renders the titration of the caustic soda possible. If the liquor to be tested contains no soda ash, some is added before the addition of the barium chloride, and the same procedure is then followed. After the alkaline liquors are removed from the goods a thorough washing, preferably at first with hot water, should be given to cleanse the fiber of all residual alkali. After being washed the goods are ready for immediate bleaching and do not require a sour as in the lime boil.

It is a practice among many bleachers to allow the cloth to lie in the kiers after the steam has been turned off, and it is thought that this steeping assists in the removal of the impurities from the cloth. Higgins finds, however, that certain of the impurities which are removed from the cloth at the boiling temperature are again attracted on cooling. In fact, as a general rule, on first heating and then cooling textile fibers in a liquid containing dissolved, suspended or colloidal matter, during the cooling there is an attraction by the fibers of the dissolved substances. Therefore, during the cooling of cloth in kiers there is a condition which interferes with the true purpose of the boiling.

6. Use of Sodium Sulfide.

Sodium sulfide has been used for kier-boiling of colored goods and apparently with considerable success; the use of this alkali, however, is attended with the danger of the formation of metallic sulfide spots,

as the sulfide will readily attack both iron and copper surfaces with the production of black iron or copper sulfides, and unless proper care is taken these black pigments may become smeared into the goods.

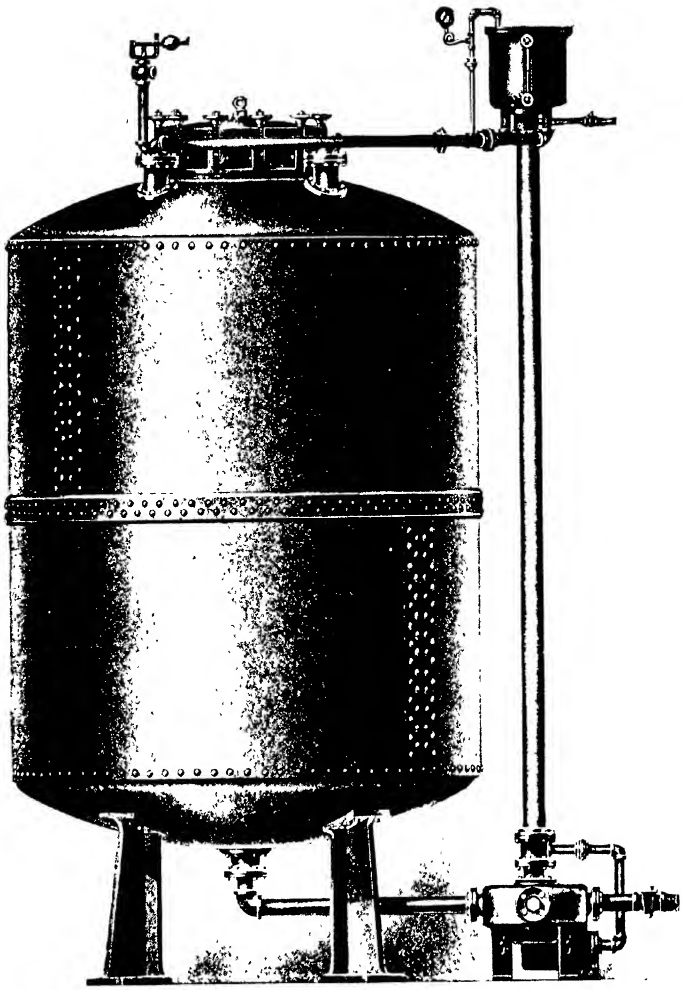

FIG. 135.—Pressure Kier with Rusden Circulator (Text. Fin. Mchy. Co.).

Again, in the use of sodium sulfide for boiling-out great care must be taken to wash out all excess of the kier liquor before the goods are brought into the chemic solution, as these sulfides are decomposed

by chlorine with liberation of sulfur in the form of a fine precipitate, and this may impregnate the fiber and lead to stains.

7. Use of Soap in Boiling-out.

Soap is not employed as much as formerly in the boiling-out of cotton, the present practice being to shorten the time by the use of stronger lyes of caustic soda in conjunction with the use of a suitable kier. In some cases, however, soap is still used, though generally in connection with caustic soda; and in some methods of bleaching, especially in the madder bleach (or Turkey Red bleach), a separate operation of boiling-out in resin soap is employed, as already explained. Some liquors, however, are largely used for finishing-off the bleaching operations, for the purpose of neutralizing traces of acid still left in the goods after washing, and for softening the cotton. When tinting is carried out, it is generally done in the soap bath.

When used in boiling-out, soap acts as a solvent or emulsifying agent for the fatty and resinous matters in the fiber, and also assists in removing the miscellaneous dirt with which the cotton becomes more or less contaminated. The soap lather causes these impurities to become loosened from the fiber so they are easily removed in the washing. Olive oil (castile) soap, olein soap, and resin soap are the principal ones employed in bleaching.

8. Preparation of Resin Soap.

Resin soap is prepared by boiling together the proper proportions of rosin and caustic soda until the former is completely saponified.

A good method for making resin soap is as follows: Take 10 parts of rosin, 2.5 parts caustic soda, and 100 parts water and boil gently for 2 hours. Test if the rosin is completely saponified by dissolving a sample of the soap in water, in which it should be completely soluble. The froth which forms on the top of the soap while boiling should be skimmed off. When completed the soap should be stringy and greasy to the touch.

In using resin soap, care should be taken that all of the rosin is well saponified, as otherwise the unsaponified portion will be deposited on the goods and stain them, though acids, as a rule, will cause this to disappear. Also resin soap is yellow in color, and if the material is not well washed, there is a liability of the yellow tinge remaining in the goods. Olein soap also is apt to leave a yellow tinge in the cotton, and in the selection of an olein soap, dark varieties should be avoided. Olive oil soap is the best as far as leaving the goods in a white condition, but it is much more expensive than the other varieties, and it is generally used only for washing the goods after bleaching. Tailfer recommends that the different soaps should be used in the following stages: Resin soap in lyes previous to chemicking; olein soap for lyes interposed between different chemics; and white olive oil soap for the last soaping. It is said that the comparative cost of the different soaps used in bleaching is about as follows:

White olive oil soap	75
Olein soap	42
Resin soap	23

The proportion of soap to be used will vary considerably with the judgment of the bleacher, but is generally about 3 pounds per

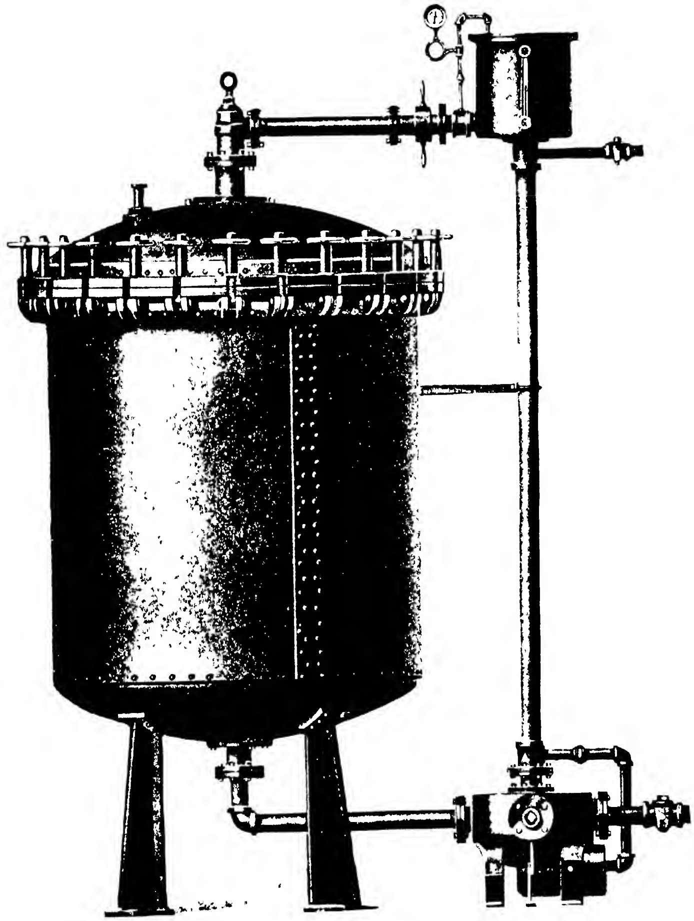

FIG. 136.—Rusden Kier for Skein Yarns (Text. Fin. Mchy. Co.).

100 gallons of lye, which would be equivalent to about 1 pound per 100 pounds of cotton. Care should be taken not to employ too high a temperature in boiling with soap lyes, as otherwise there is danger of yellowing the goods.

9. **Use of Oils.**

In some bleacheries, a heavy mineral oil of boiling point about 300° C., obtained from the distillation of bituminous shale, is added to the soda boil, or even at times to the lime boil. It is said that this effects quite a saving in the chloride of lime subsequently used. The oil, no doubt, acts as a solvent, both for the cotton-wax and the lime soap. About ½ percent of oil is used for cotton and twice that amount for linen.

Turkey-red oil or other forms of sulfated or soluble oils are frequently used in boiling-out in conjunction with caustic soda. These soluble oils readily dissolve the waxy and resinous impurities on the cotton fiber and thus allow of a quicker boil-out and at lower temperatures. Furthermore the fiber is left in a soft condition and with the use of weaker bleaching baths. The oil is simply added to the soda lye in the kier and the boiling-out process conducted as usual.

10. **Use of Malt Extract.**

Malt preparations having diastase as a basis are also used to a considerable degree for the removal of impurities from cotton. This is especially true of cloth when it is not desired to treat with boiling caustic alkali. The goods are steeped in an infusion of malt, usually overnight. The diastase enzyme acts on the starch and gums which are present in the material in such a manner as to convert them into readily soluble products, so that a subsequent washing with hot water or soap is all that is necessary to remove them from the cloth.

The natural vegetable gums of pectin matters present in the cotton also seem to be converted into soluble products by the action of malt infusions. Warps and skein yarns used for mercerizing are sometimes steeped in malt liquor overnight and then washed. This process scours the yarn in a very satisfactory manner, brings it to an absorbent condition and leaves it soft and lofty.

Piece goods containing colored borders or stripes are frequently malted instead of being boiled-out with alkali before bleaching. This prevents the bleeding of the colors. This process is especially good for vat colors which are fast to bleaching with hypochlorite liquors but which will run when kier-boiled with either milk of lime or caustic soda.

11. **Various Boil-out Compounds.**

There have been quite a number of additions suggested to the kier lyes for boiling-out and many of these have been the subject of patents at various times. Thies has studied the effect of these on the strength of boiled-out fabrics, as shown in the following summary; the boiling-out tests were conducted in an experimental kier with 1000 liters of water for 4 hours under 2 atmospheres pressure, and the figures for strength represent the mean of warp and filling in kilos.

(1) Scheurer's method:[1] 5 kg. caustic soda solid and 5 l. bisulfite (36° Bé.); strength = 57 kg.; motes and shives not completely removed; after chemicking a good white color is produced;

[1] *Ger. Pat.* 27,745.

(2) Scheurer's method: 13 kg. caustic soda solid, 2.5 kg. rosin and 5 l. bisulfite (36° Bé.); strength = 56.3 kg.; motes and shives not completely removed; after chemicking a good white color is produced;

(3) Koechlin's method:[3] 15 kg. caustic soda solid, 5 l. bisulfite (36° Bé.) and 0.8 kg. chloride of lime; strength = 59.7 kg.; motes and shives not completely removed; after chemicking the white color is not so good;

(4) Method of Thompson and Rickmann:[4] 15 kg. caustic soda solid, 5 l. bisulfite (36° Bé.) and 1 kg. kaolin; strength = 50.3 kg.; motes and shives completely removed; after chemicking the white color is not so good;

(5) Method of Bruckbaeck.[5] 15 kg. caustic soda solid, 5 l. bisulfite (36° Bé.) and 1 kg. stannous chloride; strength = 59.5 kg.; motes and shives completely removed; after chemicking the white is not so good;

(6) Method of Hertel:[6] 20 kg. caustic soda solid, 7 l bisulfite (36° Bé.) and 5 l. Turkey-red oil; strength = 59.3 kg.; motes and shives completely removed; after chemicking a good white color is produced;

(7) Method of Hertel (variation): 15 kg. caustic soda solid, 7 l. bisulfite (36° Bé.) and 15 l. Turkey-red oil; strength = 57.5 kg.; motes and shives not completely removed; after chemicking the white is not so good;

(8) Method of Hertel (variation): 10 kg. caustic soda solid, 5 l. bisulfite (36° Bé.) and 10 l. Turkey-red oil; strength = 54.3 kg.; motes and shives not completely removed; after chemicking a good white color is produced;

(9) Method of Geisenheimer: 15 kg. caustic soda solid, 5 l. bisulfite (36° Bé.) and 2 l. water glass (sodium silicate); strength = 59.0 kg.; motes and shives not completely removed; after chemicking a good white color is produced;

(10) Method of Endler:[7] 15 kg. caustic soda solid, 10 l. bisulfite (36° Bé.) and 10 kg. common salt; strength = 60.2 kg.; motes and shives not completely removed; after chemicking a good white color is produced;

(11) Method of Mahieu:[8] 20 kg. caustic soda solid and 5 l. benzene; strength = 55.2 kg.; motes and shives completely removed; after chemicking a good white color is produced;

(12) Method of Cross and Parkes:[9] 10 kg. caustic soda solid, 60 kg. water glass, 8 kg. soap, 8 kg. Rubol (sulfated oil) and 5 l. bisulfite (36° Bé.): strength = 55.8 kg.; motes and shives not completely removed; after chemicking a good white color is produced;

(13) Method of Thies: 15 kg. caustic soda solid, 5 l. bisulfite (36° Bé.) and 1 l. carbon tetrachloride; strength = 59.8 kg.; motes and shives completely removed; after chemicking the white color is not so good;

(14) Method of Thies: 15 kg. caustic soda solid, 5 l. bisulfite (36° Bé.) and 5 l. alcohol (denatured): strength = 59.5 kg.; motes and shives completely removed (best of all tests); after chemicking, the white color is not so good;

(15) Method of Weber: 15 kg. caustic soda solid, 5 l. bisulfite (36° Bé.) and 3 l. glycerin; strength = 56.7 kg.; motes and shives completely removed; after chemicking the white color is not so good.

While these results are interesting in a comparative manner, they should not be taken as a definite determination of the proper character of the boiling-out compound to be used, as they have all been carried out with the idea of introducing sodium bisulfite as an ingredient in the kier liquor for the purpose of preventing tendering of the goods through oxidation in the kier. Before definite conclusions can be drawn in this regard it would be necessary to carry out much more extensive tests under set conditions of practice and with the introduc-

[3] *Ger. Pat.* 25,804 and 27,745.
[4] *Ger. Pat.* 32,704.
[5] Patented 1827.
[6] *Ger. Pat.* 75,435.
[7] *Brit. Pat.* 14,252.
[8] *Ger. Pat.* 61,668.
[9] *Ger. Pat.* 121,787.

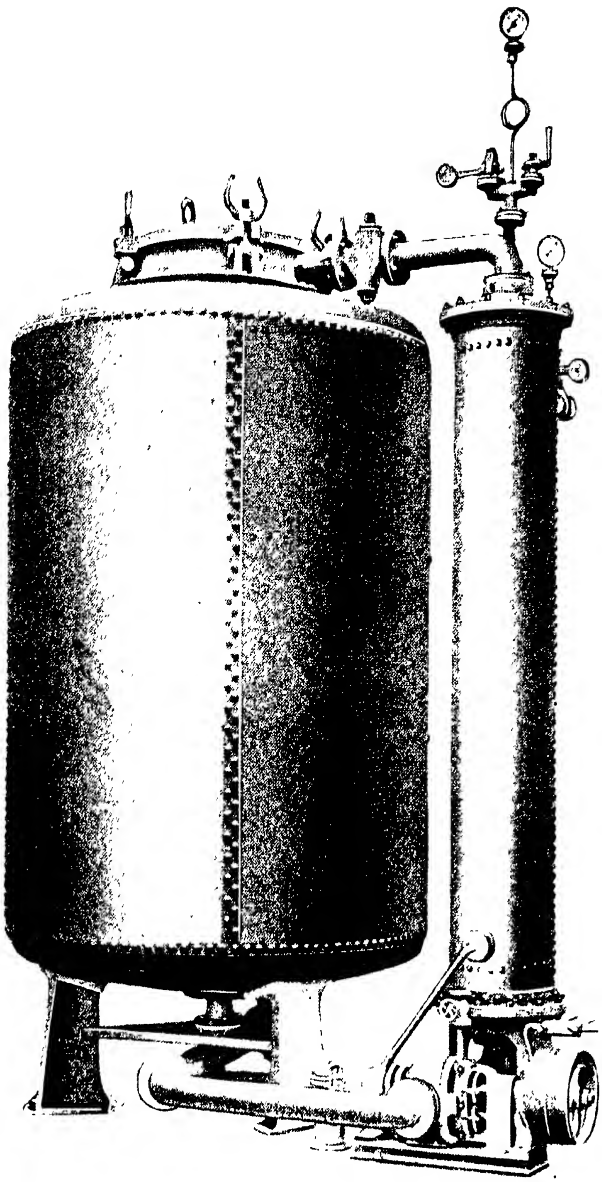

FIG. 137.—High Pressure Kier (German Type).

tion of single variants for the purpose of estimating their relative effect on the strength of the material. From the results obtained in practical kier-boiling it would seem that after boiling-out, the goods are somewhat stronger than before, provided the operation has been ordinarily conducted with care and skill. From actual figures obtained in practice this increase amounts to 5 to 15 percent. Koehler has found that when the concentration of the caustic soda solution exceeds 3° Bé. the tensile strength of the material no longer shows an increase, but begins to show a decrease above this strength of alkali. There are so many conditions in the boiling-out of cotton materials that will effect the strength that it makes a rather complex problem. The nature of the fiber, the staple, the twist of the yarn, the nature of the weave and construction of the fabric, the kind of chemicals used in the kier liquor, the strength of the alkalies employed, the proportion of the cotton mass to the kier liquor, the temperature of boiling, the pressure, the length of time in boiling, the manner of the circulation of the liquor during boiling, the design of the kier, the use of live steam or indirect heating of the kier liquor, the nature of the water employed in washing are all factors which would have to be systematically investigated in order to arrive at a definite conclusion as to the most satisfactory method of boiling-out with respect to the preservation of the strength of the material under treatment.

12. Amount of Alkali for Boiling.

As to the amount of alkali to be employed in the caustic soda boil this will vary somewhat with the character of the goods undergoing treatment as well as the type of kier employed. In general, it may be stated as 2 to 5 percent on the weight of the fabric. The volume of the kier liquor must always be sufficient to completely cover the goods in the kier after complete saturation of the fiber and to furnish sufficient surplus to permit of proper circulation. An excessive quantity of liquor is unnecessary and should be avoided, as it may cause the goods to float in the kier and thus become entangled. It has been found by experience that it will require about 75 gallons of liquor in the kier for 100 pounds of goods; this figure, however, will vary with certain limits depending on the nature of the goods and the density with which they are packed in the kier. The amount of liquor originally run into the kier to start with will also depend on whether live steam is used for heating or whether the heating is done indirectly in an outside boiler. In the former case, proper allowance must be made for the continual addition to the volume of the liquor from the condensed steam. The injector type of kier which uses live steam for both heating and circulation condenses quite a large proportion within the kier; this will naturally decrease the concentration of the alkaline liquor as the boiling proceeds, and allowance must be made for this. Also if too much condensation takes place from one cause or another, the volume of the kier liquor may become so great as to float the goods. On this account it is not well to start boiling the kier with steam at too low a pressure, as the ratio

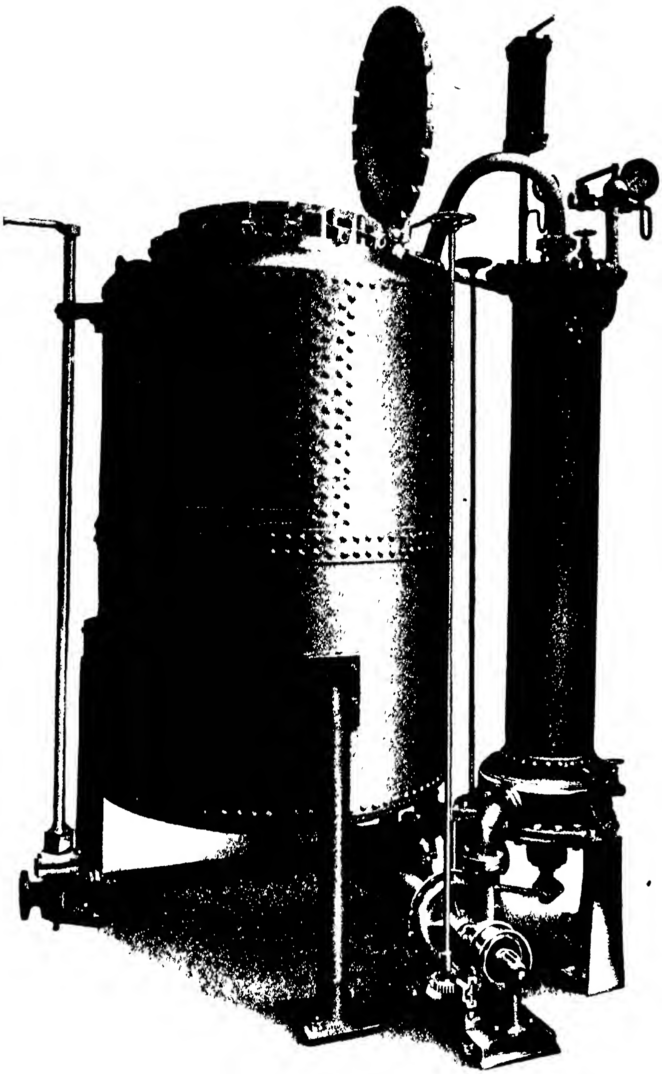

FIG. 138.—High Pressure Kier with Centrifugal Pump and Multitubular Heater (English Type).

of the water condensed to the steam content is high, and if the kier is started with a volume of liquor small enough to allow for the increase in volume through condensation at the end, the quantity will usually be insufficient to produce a good circulation and completely cover the goods. While, on the other hand, if sufficient volume of liquor is used to start with by using a low pressure steam the condensation will be so great that before the end of the boil is reached the kier will become flooded with a diluted liquor. It is always necessary to remember, however, that under any circumstances the kier should not be boiled without the cotton being completely covered by the liquor, for otherwise the hot steam will come into direct contact with the alkaline goods, and this will very likely cause serious damage, both with respect to tendering the fiber and discoloring the cotton.

13. Temperature of Kier-boiling.

The temperature of kier-boiling, of course, is determined by the type of kier used; in the case of open kiers this temperature cannot get above the boiling point of the alkaline liquor used. It may be somewhat above the boiling point of water (212° F.), though generally such excess, if any, will be very slight. With closed pressure kiers, such as are used almost entirely at the present time, the temperature of the boiling will correspond to the pressure of the steam within the kier, and consequently may reach a point considerably above that of boiling water. As this point is of considerable interest to the bleacher, there is given the following table showing the relation between the steam, pressure and the temperature.

RELATION BETWEEN STEAM, PRESSURE AND TEMPERATURE

Pressure in Atmospheres	Actual Kier Pressure, Lbs	Temperature of Steam Cent	Fahr.
1.00	0.	100.0	212.0
1.25	3.7	106.0	223.0
1.50	7.3	111.0	231.0
1.75	11.0	116.5	241.0
2.00	14.7	121.0	250.0
2.25	18.4	124.0	256.0
2.50	22.0	127.0	261.0
2.75	25.7	131.0	268.0

It is generally held that cotton cannot be heated above 130° C. without serious danger of decomposition of the fiber resulting in discoloration and weakening, but while this point may have become established as the critical temperature for cotton heated in the presence of air and alkali, it is by no means certain the same holds true for the conditions of heating as they exist in the kier. In the absence of air it is probable that cotton may be heated to a much higher temperature than this if immersed in a solution of caustic soda, and consequently it may be possible to run the pressure and corresponding temperature of the kier to a considerably higher point. This question, however, still awaits experimental determination before a definite conclusion can be reached.

Schwalbe in commenting on the action of sodium hydrate and water under pressure on cotton cellulose[10] states that only celluloses which contain oxycellulose show the property of producing hydrocellulose by heating under a pressure of 20 atmospheres. Pure, nor-

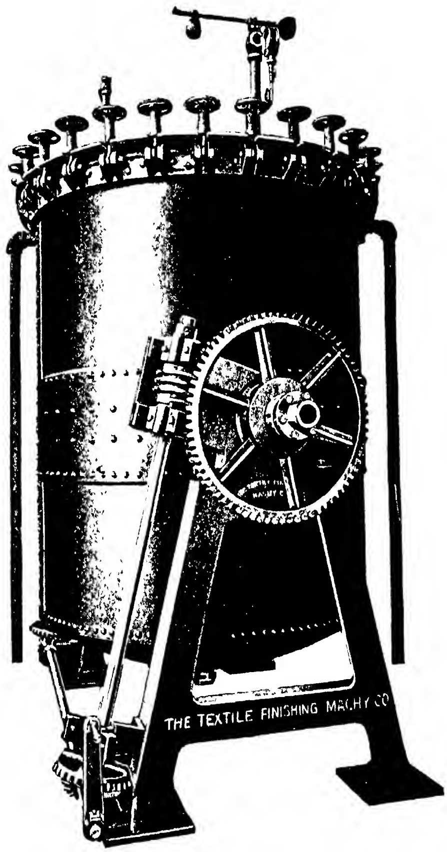

FIG. 139. Pressure Kier with Tipping Arrangement (Text. Fin. Mchy. Co.).

mal cellulose (cotton) suffers but a very slight hydrolysis; at temperatures above 100° C. dehydration appears to take place, and the "hydration value" decreases with increase of temperature. The proportion of products soluble in water increases only very slowly with the increase in temperature up to 150° C., but it increases very rapidly above this temperature. On heating with sodium hydrate under pres-

[10] *Chem. Zeit.*, 1910, p. 551.

sure, the copper reducing power of the cellulose, which appears under the action of sodium hydrate at 100° C., disappears when the concentration of the lye is 1 to 2 percent; with lyes of higher concentration (3 to 5 percent) the copper reducing power does not disappear until a temperature of 135° C. is reached. The degree of hydrolysis, as expressed by the copper reducing power, is at a maximum with a 4 percent lye; lyes of 3 and 5 percent both having a weaker action. The solubility of cotton cellulose in sodium hydrate at the ordinary temperature decreases as the concentration of the alkali is increased, and this is also the case at 100° C. At a temperature of 150° C. the solubility in lyes of 1 to 5 percent concentration ranges from 5 to 7 percent. Above 150° C. the solubility of the cellulose increases with extreme rapidity. Consequently the temperature of 150° C. may be regarded at the decomposition temperature of cotton cellulose. As in the case of water, sodium hydrate also appears to produce dehydration at temperatures above 100° C., since the "hydrolysis value" decreases with increase of temperature. Schwalbe also states that Egyptian cotton appears to possess a higher degree of hydration than American cotton.

14. Water Used in Kier-boiling.

The water employed for preparing the kier liquor should be as soft as possible when the caustic soda boil is used; if hard water is used lime and magnesia will be formed by the interaction of the metallic salts with the caustic soda, and these will combine with the fatty acids of the cotton to form insoluble metallic soaps which can only be subsequently removed by decomposition with an acid liquor or sour. Trotman and Pentecost[11] have shown the difference in the character of the boil-out with caustic soda when using hard water on the one hand and soft water on the other. The hard water contained 40 parts hardness per 100,000. The results showed that with soft water 23 percent more of the fats were removed. It is also claimed that soft water is better to use than merely softened water, as in the latter case neutral salts, such as sodium chloride and sulfate, may have a retarding effect on the action of the alkali in the boil-out. Water containing iron in excess of 0.05 part per 100,000 should be avoided for boiling-out, as this impurity is very liable to effect the purity of the color in the bleached goods. Iron may be introduced under certain conditions by the condensed steam that may accumulate in the kier, and under no circumstances should water from condensed steam be stored in iron tanks and then used as a source of hot water for washing the kier boiled goods, as such water will become highly contaminated with iron, due to the great solubility of the latter in the pure condense water.

15. Washing in Kier.

After boiling with caustic soda the goods should be washed first in the kier so as not to be exposed to the action of air while still saturated

[11] *Jour. Soc. Chem. Ind.*, 1910, p. 4.

with the alkaline liquor. In other words, the goods should not be taken from the kier until they are thoroughly cooled and only traces of alkali are left in the fiber, otherwise there is danger of oxycellulose being formed leading to tender and discolored spots and streaks. Also, if the cotton, still containing the kier liquor of caustic soda, is left exposed to the air for any length of time, especially in the hot condition, the surface liquor will become highly concentrated by evaporation, and this may ultimately reach a point where the caustic soda will become sufficiently concentrated to produce a mercerizing effect on the cotton, causing both severe shrinkage and a material alteration in its dyeing properties. Furthermore, if not washed directly in the kier, it will be more difficult subsequently to remove the various impurities from the cotton, and so-called kier stains will be liable to develop which are hard to get rid of. It has been mentioned that the chief impurities in the fiber which are rendered soluble by the action of the alkali in the kier boil consist of so-called pectin bodies which form jellies on cooling; that is to say, a very small proportion of pectin in solution on cooling will give a rather stiff colloidal mass and thus become as a precipitate in the fiber. If this is exposed to the air or allowed to harden by evaporation it will become very difficult to wash out, and the retention of this matter by the cotton will give all the effects of an imperfect boil.

16. Faults in Boiling-out.

Faults in the boiling-out of cotton may arise from kier stains due to improper circulation of the liquor or improper packing of the material in the k er or from rust in kiers which have not been properly cleaned and cared for. The use of dirty water or water containing iron will also develop kier stains.

The necessary conditions to secure a complete and satisfactory boiling-out, according to Trotman and Thorp, are as follows:

(1) The use of suitable water;
(2) Proper packing and good circulation of the liquor in the kier;
(3) Absence of air and oxygen from the kier;
(4) The use of sufficient alkali;
(5) The complete removal of the lye immediately after the boil;
(6) Avoidance of direct contact of the goods with steam pipes;
(7) The use of pure chemicals;
(8) Maintaining the kier in a clean condition.

Other defects in boiling-out arise from the use of too strong lyes, too high temperatures or too prolonged a boiling, in which cases the fiber may become injured. Allowing the goods to cool in the waste lye is also liable to develop stains and uneven streaks. The exposure of the goods to the action of air when saturated with the hot lye will tend toward the formation of oxycellulose, and this leads to the tendering of the goods and the formation of stains. This is especially liable to be the case when open kiers are used, and the top layer of the goods is incompletely submerged beneath the boiling-out liquors. In the use

of closed kiers care should be had that all air is replaced by steam before the actual boiling-out is commenced.

A fault which is sometimes found in kier boiling is the formation

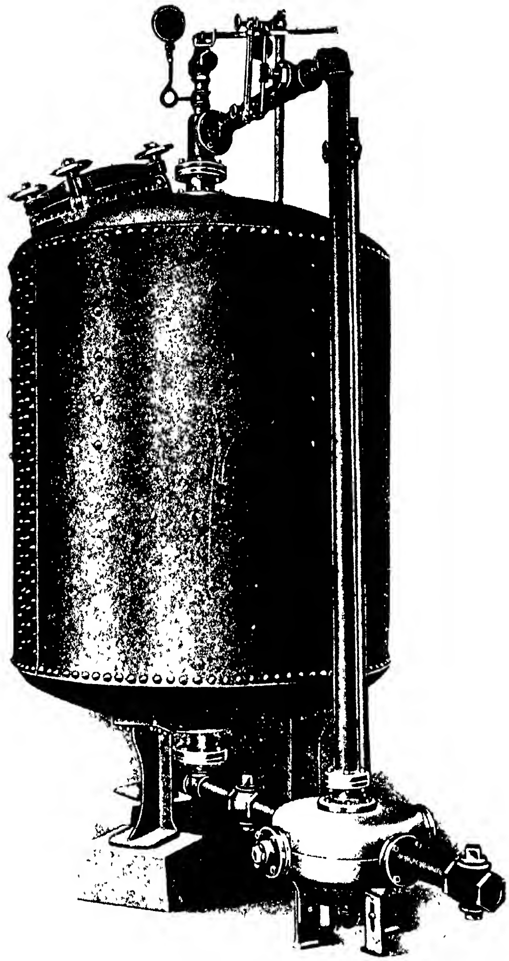

FIG. 140.—Rusden Kier with Off-Center Opening (Text. Fin. Mchy. Co.).

of "shot holes" in the cloth. The cause of this defect is not thoroughly understood; by some it is attributed to the action of steam attacking goods through the false perforated bottom of the kier; by others, to a bad circulation due to hard places caused by improper

folding down of the cloth. Trotman suggests that it may be caused by friction of the cloth against rough spots on the side of the kier resulting from the accumulation of lime deposits. These deposits are liable to form in kiers used for lime boiling if the sides are not frequently scraped down; also it is advantageous to alternate the lime and soda ash boils in the same kier as this will materially assist in the removal of the rough projections.

Trotman and Pentecost [12] consider the absence of air and oxygen as the most essential condition to good results in caustic soda boiling. Not only do residues of air in the kier cause oxidation of the fiber, but, by expansion, cause air bubbles which protect the cotton from action of the alkali and thus produce local imperfections in the boil-out.

17. Loss in Strength on Boiling-out.

With regard to the loss in strength of the cotton which may be brought about by the action of boiling-out, Scheurer [13] found from carefully conducted experiments that if all air is excluded in the boiling-out a treatment for 8 hours at 150° C. with a caustic soda lye did not produce any perceptible decrease in tensile strength of the cotton fabric. It was found, however, that the presence of even very small amounts of air produced a weakening effect, probably due to the formation of oxycellulose. Scheurer found that it was necessary in his tests even to treat the cotton first with alcohol in order to eliminate the air held in the pores of the fiber in order to obtain the ideal condition.

Trotman and Thorp point out that the danger of producing oxycellulose is quite as great with the lime boil as it is with the caustic soda boil, and, in fact, complaints of tendering are usually far more common where the lime boil is used. These, however, are generally caused by a local "burning," owing to careless slaking or the use of unsuitable lime, for if lime be badly burnt or contains much magnesia, it slakes very slowly, and the unslaked particles may pass into the kier liquor, and, becoming entangled in the cloth, may become the cause of local tendering or "burnt" spots.

A very systematic investigation of this matter was undertaken by Theis.[14] Proceeding upon the idea that the weakening effect in boiling-out was caused by oxidation in the kier, experiments were made with the use of reducing agents added to the kier liquor for the purpose of neutralizing any oxygen present and thus avoiding the possibility of the formation of oxycellulose. For this purpose sodium bisulfite was used. The following table shows the main results of these experiments.

Kier Treatment	Mean Strength Warp and Filling
Raw fabric	100.0
High pressure, soda ash, 8 hours	83.0
High pressure, lime, 8 hours	82.2
High pressure, 1 soda and 2 lime	79.1
Open kier, caustic soda 4° Bé., 1 hour	78.0

[12] *Jour. Soc. Chem. Ind.*, 1910, p. 4.
[13] *Mulhausener Berichte*, 1888.
[14] See Theis, *Breitbleiche*.

Kier Treatment	Mean Strength Warp and Filling
Boiling 5 hours at 14 lbs. pressure:	
Caustic soda 4° Bé. alone	67.1
Same, with 10 gms. bisulfite to liter	77.2
Caustic soda 6° Bé. alone	58.6
Same, with 10 gms. bisulfite to liter	60.5
Caustic soda 8° Bé. alone	53.6
Same, with 10 gms. bisulfite to liter	59.5
Caustic soda 10° Bé. alone	57.4
Same, with 10 gms. bisulfite to liter	63.6

Other interesting tests made by Theis are shown in the following table, an experimental kier being used with 1000 liters of water and under the conditions as stated:

BOILING 4 HOURS UNDER 2 ATMOSPHERES PRESSURE

Kier Liquor	Mean Strength Warp and Filling
Raw fabric	100.0
Boiled-out usual manner, high pressure, 10 hrs.	95.1
15 kg. caustic soda solid 5 l. bisulfite (36° Bé.) 1 l. carbon tetrachloride	107.7
15 kg. caustic soda solid 5 l. bisulfite (36° Bé.) 5 l. alcohol	107.2
20 kg. caustic soda solid 7 l. bisulfite (36° Bé.) 5 l. Turkey-red oil	106.8
20 kg. caustic soda solid 0.5 l. benzene	99.5

Tests conducted under the same conditions of kier liquor but boiling for 1 hour under a pressure of 8 atmospheres gave proportionate but slightly lower results. As a result, however, of various tests, it is advised not to use a kier temperature of over 130° C., as above this temperature the operation becomes dangerous to the strength of the material.

According to Trotman and Pentecost [15] the use of caustic potash will materially decrease the time of boiling-out as compared with the use of caustic soda, and this substitution may be made where the extra cost of the alkali is more than compensated by the gain in time. Experiments have shown that in any length of time less than that necessary for the complete action of soda, potash will always remove about 20 percent more than soda when used in equimolecular solutions.

The relative scouring values of different alkalies used in kier-boiling may be rated by a comparison of the amounts of impurities removed from the cotton under exactly similar conditions. Trotman and Pentecost [16] give the following results of experiments on this feature:

[15] *Jour. Soc. Chem. Ind.*, 1910, p. 4.
[16] *Idem.*

Alkali Used	Loss in Percent
Caustic potash	5.00
Caustic soda	4.40
Sodium carbonate	3.70
Sodium borate	2.80
Sodium silicate	2.40

The danger of mercerization of the goods in boiling-out seems to be much exaggerated if the conditions of the process are clearly considered and compared with the conditions that are known to be necessary for mercerization. In the lime boil there is little or no chance of mercerization taking place as the alkali employed in this case is chiefly soda ash, and even where caustic soda is employed as an adjunct, its concentration is far too low. In the caustic soda boil itself it can hardly be understood just how mercerization can take place, as in the first place, the concentration of the alkali is far below the mercerizing point, and also mercerization proper does not occur at high temperatures such as employed in kier-boiling. The only possibility, apparently, of mercerizing being possible is the use of cold concentrated caustic soda solution as an addition to the kier liquor, so that this mercerizing liquor comes in contact with the cotton before there is a chance for its proper dilution. Such a method of adding the caustic soda liquor to the kier, however, is a very improper one and is not liable to be practised in any successful bleachery. On the whole, it may be said, therefore, that the mercerizing bugbear in kier-boiling is more the product of an unscientific imagination than a real fact.

Chapter XV.

The Boiling-out of Cotton (*Cont.*).

1. Apparatus Used in Boiling-out.

The principal apparatus employed by the bleacher in the processing of his goods is the kier. This is really nothing more than a boiler in which the yarn or cloth is boiled with the alkaline liquor. The construction and types of kiers have undergone many changes since this method was first brought into use. Illustrations of some of the early forms of these kiers have been presented to the attention of the reader in the preceding pages. At first a simple wooden vat was used in which the goods were placed to be treated with the hot liquor, and the alkaline lye itself was heated independently in a copper or iron kettle by the direct heat of a fire. The hot liquor was then ladled out by hand and poured over the goods, and after passing through the latter ran off at the bottom of the kier back into the heater. This type of apparatus is described by Berthollet.[1] The deficiencies of such an apparatus were, of course, very soon made apparent; in the first place, it was not possible to keep the liquor in the kier at a temperature anywhere near the boiling point. The best that could be done in this respect, according to Berthollet, was to maintain a temperature of about 190° F. Also there was poor circulation and the goods were subjected continually to the action of the air. In those days the liquor employed consisted of a solution prepared by leaching out wood ashes, and was therefore mostly potassium carbonate. As this was rather costly, however, later on milk of lime was used. Another form of primitive apparatus was one in which a kettle or boiler of metal was used for heating the lye directly over a fire, and into this kettle there could be raised and lowered a basket made of strong reeds and which contained the goods to be treated (see Figure 2). This is described by Tenner in his book entitled *Anleitung mittelst dephlogistisierter Salzsäure zu Bleichen*.[2] By this means the liquor could be maintained at the boiling point, and furthermore by moving the basket up and down in the kettle a better circulation of the liquor through the goods could be obtained. A very similar form of apparatus is described by Pajot des Charmes.[3] A distinct improvement is to be found in the apparatus of William Floyd.[4] In this case a copper boiler heated in a direct fire was used; this contained the lye and was connected by pipes at top and bottom with the adjoining wooden kier containing

[1] *Anfangsgründe der Färbekunst*, Berlin, 1806.
[2] *Anleitung mittelst dephlogistisierter Salzsaure zu Bleichen*, Leipzig, 1793.
[3] *Die Bleichkunst*, Breslau, 1800; see also figure 105
[4] Described in *Brit. Pat.* 2073 of 1795, and shown in figure 106.

the goods. An overflow or safety pipe was arranged by running a vertical pipe up from the top of the boiler. By this arrangement the liquor circulated through the kier, going in at the top and coming out at the bottom, very much in the same manner as to be seen at the pres-

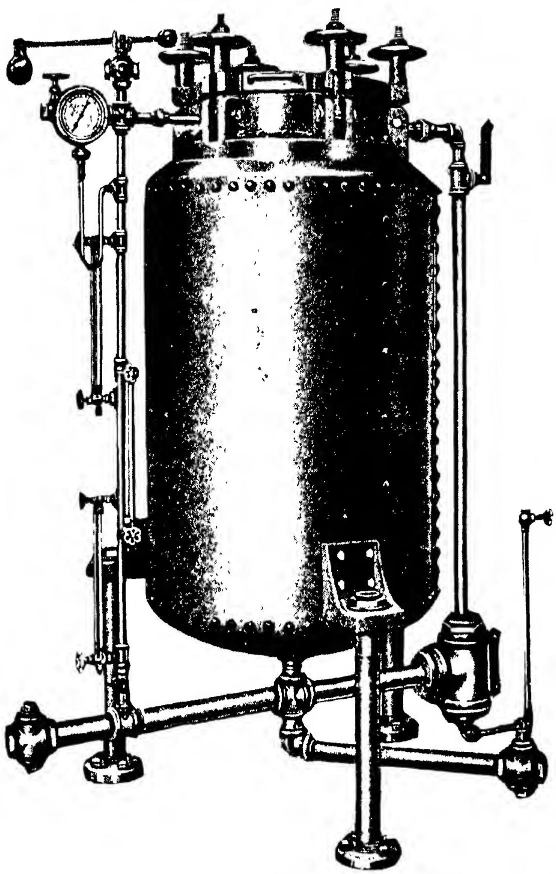

FIG. 141. Small Special Kier for Experimental Boiling (Text. Fin. Mchy. Co.).

ent time in domestic hot water boilers heated from without by a gas flame in contact with a long coil of copper pipe. A very similar type of kier is later described by Persoz [5] as operating in the bleachery of Dollfus Mieg in Mulhausen (see Figure 107), it being so constructed as to have a kier on each side of the boiler.

[5] *Traite theorique et pratique de l'impression des tissues,* Paris, 1846.

2. Pump Circulation in Early Kiers.

A rather primitive type of kier, employing, however, a mechanically operated pump, is described by Samuel Parkes.[6] An outside boiler heated by a direct fire was used and the liquor simply ran into the kier by gravity (see Figure 108); a pump, however, was used to carry the liquor from the bottom of the kier back into the boiler. The first time apparently that a central vomit pipe was used in a kier is in the description of Kurrer.[7] This apparatus consisted of a wooden kier erected directly over a copper boiler placed over an open fire; the kier had a perforated bottom through the center of which rose a pipe extending through the kier and with its lower end dipping into the heated liquor in the boiler underneath (see Figure 109). Another form of early kier provided with a pump for the circulation of the liquor is that of Widmer and described in the book by Berthollet quoted above (see Figure 110); in this type of kier the kier proper is located directly over the boiler as in the last form described. A pipe runs down through the center of the kier and into the boiler, and this pipe is so operated by a pump as to draw the hot liquor up to the top of the kier so as to percolate through the goods and then run back into the boiler through the perforated bottom of the kier. The kier of Kurrer was modified by Kreisig[8] using an all-metal boiler and kier, forming really one piece of apparatus; the boiler being the lower part of the kier and being placed directly over a fire (see Figure 109). This is probably the first instance of a metal kier being used. The internal center vomit pipe with a distributing head at the top was also employed.

3. Use of Steam for Circulation.

The use of steam for circulating the liquor by means of an injector was not introduced until later, though even the early type of this kier was constructed entirely of wood. About 1790 a French chemist Chaptal made the observation that if cotton goods were saturated with an alkaline liquor and then steamed the impurities could be more easily removed than by simply boiling in the liquor. This idea was probably the basis on which John Turnbull devised a method and apparatus for boiling cotton.[9] The cotton was saturated with the lye and then placed in an apparatus in which it was subjected to the action of live steam. O'Reilly[10] also took up Chaptal's idea and constructed an apparatus which consisted essentially of a heater or sort of oven in which were two reels on which the yarn or cloth could be wound and transferred from one to the other. The goods were impregnated with the lye and then worked back and forth in this oven which was also provided at its bottom with a shallow tank or boiler heated by a direct fire underneath the goods, being thus subjected to the action of steam as they were unrolled from one reel to the other. It was found, however, that in order to obtain a satisfactory boiling-out the treatment had to be continued

[6] *Chemical Essays*, vol. 4, London, 1815
[7] *Die Kunst vegetabilische Stoffe zu Bleichen*, Nurnberg, 1831.
[8] *Der Zeugdruck und die damit verbundene Bleicherei und Färberei*, Berlin, 1834.
[9] *Brit. Pat.* 2445 of 1800
[10] *Essai sur le blanchiment*, Paris, 1801.

for 20 to 30 hours. Hermbstadt[11] adopted this same process, but modified it so that the cloth was made to pass through the boiling lye in the bottom of the oven and then was carried up and over a reel, and then reversed in its motion by another reel. This method of operation was found to cut down the time necessary for treatment to about 4 hours. These methods of boiling-out were probably the first instances of treatment of the goods in open width form rather than in a packed mass or in rope form, and are interesting in the study of the later development of the open-width processes of boiling-out and bleaching as is shown in the Mather & Platt type of kier.

Theis,[12] in reviewing the early development of the art of boiling-out and bleaching states that at the beginning of the 19th century the following methods of boiling-out were known and practiced: (1) Pouring of the hot lye over the goods contained in an open kier or tank, the operation being conducted by hand; (2) the use of a mechanical pumping device for circulating the lye, as shown in the apparatus of Widmer, Floyd, Neumann and Parkes; (3) steaming of the goods impregnated with the lye in the open-width (Chaptal) or in the rope form (Turnbull) and under a slight pressure. This seems to be the first attempt to employ pressure in boiling-out; (4) alternate steaming and treatment with the lye and under slight pressure in a closed vessel as in the process of Hermbstadt.

4. Modern Apparatus.

As engineering science developed many improvements were made in the construction of boiling-out kiers. In the first place, the use of a direct fire for heating the liquor was soon dispensed with and the heating was done by means of high pressure steam provided from an independent boiler. Also the use of wooden kiers was abandoned for the stronger and larger iron or steel kiers. The methods for circulating the liquor were also much improved, and various mechanical devices were introduced to facilitate the handling of the goods, and even in some cases the entire structure of the kier was changed so as to permit the goods being boiled-out in the open-width form (as in the Mather & Platt kier). With the use of steel construction it became possible to use closed kiers and carry out the boiling at a high pressure and at a consequently higher temperature, a feature which allowed of much saving of time and a more complete boiling-out. At the present time kiers are almost entirely of the closed pressure type.

5. Methods of Heating Kiers.

With regard to methods of heating, modern kiers may be divided into three types: (a) heating by direct steam within kier, (b) heating by indirect steam (closed coil) within kier, and (c) heating by steam-chest outside of kier. The method of heating by direct steam has the advantage of simplicity of construction especially when the heating is combined with the function of circulation, as when a steam injector

[11] *Allgemeine Grundsätze der Bleichkunst*, Berlin, 1804.
[12] *Die Strangbleiche baumwollener Gewebe*, Berlin, 1905, p. 12.

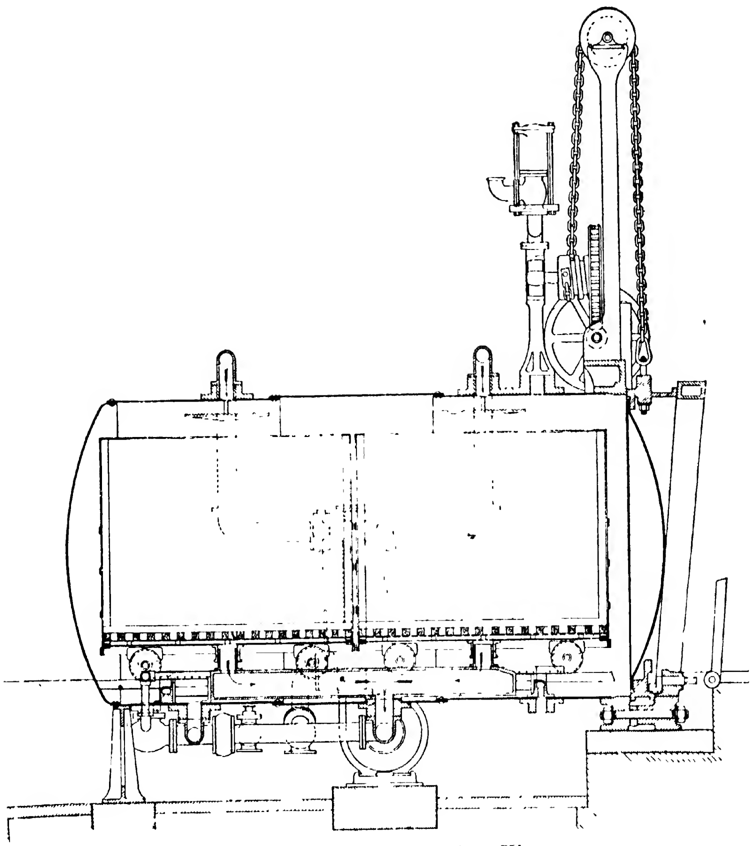

FIG. 142.—Diagram of Mather Kier.

is used. This method, however, has the disadvantage of bringing the goods into more or less direct contact with highly heated steam, and this may cause injury to the cotton; also the direct introduction of steam with its consequent condensation is continually diluting the liquor in the kier. In order to avoid the bad features just enumerated, instead of heating by steam directly introduced with an open coil, another type of kier uses a closed steam coil located in the bottom of the kier and beneath the false bottom so that the highly heated pipes may come in contact only with the liquor and not with the cotton material. This method of heating, of course, precludes the possibility of using an injector method of circulating the liquor, and the latter has to be done by a pump or other means. With the closed coil system of heating the time required to bring up the temperature is longer, but

there is no dilution of the liquor nor danger of locally overheating the cotton. The outside type of heater also uses a closed steam coil but situated in a separate chest or boiler usually in a vertical cylinder placed alongside the kier. This method of heating has also to be combined with circulation by means of a pump or a vacuum chest. The outside method of heating seems to be growing in favor and doubtless offers certain advantages of control which make it more desirable than methods of heating within the kier. In order to economize heat the kier together with the various pipes and accessories for steam and hot water, should be covered with a suitable insulating material to prevent excessive heat losses by radiation.

6. Methods of Circulating Liquor; Injector System.

With respect to methods employed for circulating the liquor, modern kiers may be classified as follows: (a) injector kiers, (b) pump system, and (c) vacuum system. The injector principal of circulation is usually considered the older form, but it was really preceded historically by a method of pumping, although since the introduction of the pressure kier it may be said that the injector method of circulation was at first used and the pump system was not introduced until later in connection with this type of kier. The principle of the steam injector is shown in Figure 111. The high pressure steam is introduced through a narrow conical opening and coming in contact with the liquor in a slightly expanded chamber gives to it to some extent the great velocity of the steam, and at the same time owing to the rapid condensation of the steam by the liquor at the extremity of the cone, forms a continuous column of liquor with the high pressure of the steam back of it. A modification of the injector is the old form of puffer pipe (see Figure 112), where a blast of steam is simply introduced into a pipe filled with liquor, with the result that the pressure of the steam blows the liquor up through the pipe. The same method is also employed in the old type of kier using a closed steam coil for heating underneath a perforated dome and so arranged that the quickly heated liquor is given sufficient local pressure to force it up a central vomit pipe to the top of the kier (see Figure 113). As the force of circulation in this type of kier was not very great and the liquor could not be lifted to any considerable height, the kier was usually made rather flat in shape.

In kiers of the type with inside injectors the pipes for the steam and the kier liquor should be at least of the size given below:

Flow of liquor per hour in liters	Steam pipe in mm.	Water pipe in mm.
7,500	40	50
10,000	50	60
15,000	50	80
30,000	60	100

Sharp bends in pipes should be avoided in order to reduce the friction of circulation. The kier should be filled as completely as possible with liquor. Closed kiers must be provided with an efficient safety-valve

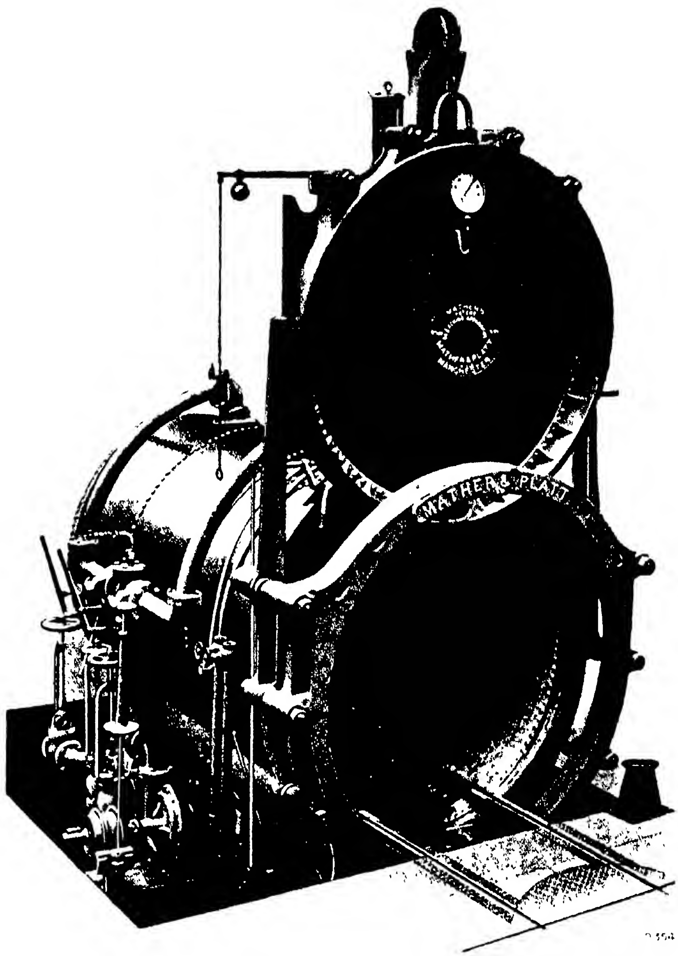

FIG. 143.—Outside View of Mather Kier.

so arranged that the internal pressure cannot reach a point greater than one atmosphere lower than the steam pressure. Care should be taken that the safety-valve is always in working condition.

The injector system of circulation when used in connection with open kiers will not raise the liquor above the boiling point, but when used with closed kiers a temperature considerably above the boiling point can be reached. In the latter case the pressure of the steam

supply should be at least one atmosphere higher than the pressure in the kier.

One objection that has been raised to the steam injector type of circulator is the rather large expenditure of steam required to carry over the liquor, this being especially pronounced in the case of high pressure kiers. Also the steam is continually condensing in the kier liquor and thus diluting its strength. Another objection is due to the fact that when the liquor gets up to about the same temperature as the steam the result will be that only foam and very little actual liquor will be carried over. The steam injector therefore to work effectively needs a supply of steam at a pressure very much higher than that at which the kier is worked. The puffer pipe and the coil heater type were usually only adapted to either a low-pressure kier or better an open kier.

A rather unique form of injector kier was that of Taylor and made by Mather & Platt (see Figure 123). In this apparatus the injector was more of the order of a puffer pipe and was located in a separate small kettle outside the kier. This kier was used in the early 70's in England, but has now gone out of style.

7. The Pump System.

The pump system of circulation may be operated in two ways, either by the use of a centrifugal pump or with a plunger pump. The former is the one generally used. There are certain difficulties in this system which have to be overcome by well-studied engineering technique; in the first place as the liquor operated on is at a high temperature, the expansion of the pump parts is liable to give trouble; in the second place, since the pull of the pump is really due in some degree to its creating a vacuum, when a very hot liquor is in question there will be produced a considerable amount of vapor which will be blown over by the pump rather than a continuous stream of liquor. This difficulty, however, is perhaps less in the case of the centrifugal pump than with the plunger pump. The circulation by centrifugal pump is becoming a popular type of kier and practical results seem to indicate a high degree of efficiency.

8. The Vacuum System.

The vacuum system of circulation (such as is employed for example in the Jefferson type of kier) uses a rather unique principle for the automatic making and breaking of a vacuum produced in an outside steam chest, so that liquor is drawn into this chest and then blown over by direct steam pressure, the steam in this manner also acting to heat the liquor. A kier devised by Trotman and Thorp also works on this same general principle. By the use of an electrical device for opening and closing the steam valves the Jefferson kier becomes completely automatic in its operation.

9. Kiers for Loose Cotton.

The type of machinery employed for the boiling-out of cotton will naturally depend on the character of the goods being treated. In the

case of loose cotton the boiling-out (as well as the succeeding operations of bleaching) is conducted in a closed apparatus in which the liquor is circulated through the material by means of a pump. This machine consists of a cylindrical iron vat provided with a perforated false bottom and a perforated cover. The cotton is packed into the vat as uniformly as possible, then the cover is placed in position and screwed down securely. A circulating pump is connected with the space beneath the perforated false bottom and also to the space above

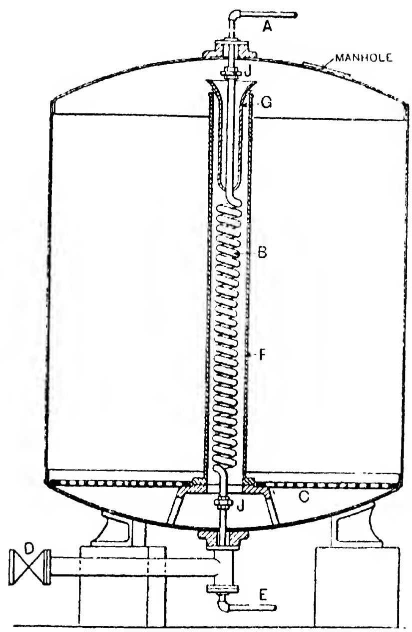

FIG. 144.—Patent Kier with Special Heater (English Type).

the cover, so that the liquor in the vat is forced in at the bottom and up through the cotton and then taken off again at the top. Loose cotton stock will pack down more firmly in a kier than either yarn of cloth, and consequently the mass will be less easily penetrated by the liquor, for when the cotton is impregnated with the hot caustic soda solution the fiber becomes quite plastic and gummy in consistency, which makes it consolidate to almost a solid mass. On this account kiers for boiling out loose cotton should be of a moderate height so as to present less thickness of material for the liquor to penetrate; or if the usual proportion of height of kier is used a higher pressure must be employed to obtain good circulation. Loose cotton is extensively boiled-out for the

preparation of absorbent cotton for surgical purposes and also for the making of gun-cotton.

Besides the raw loose cotton which is boiled-out for bleaching purposes there is a large amount of cotton waste of different degrees of purity which is also boiled-out for use in making surgical absorbent cotton, as a basis for celluloid, and for cotton wadding and batting used in upholstery work. This cotton waste sometimes contains a considerable amount of mineral oil and dirt. Cotton linters (which are the short low-grade fibers obtained in the second ginning of the cotton-seed) are also extensively used for the above-named purposes and must be subjected to the boiling-out process. Linters contain a large amount of broken seed-hull and dirt, as well as a large proportion of oil. To obtain good clean products from these low-grade materials it is necessary to carry out a very thorough boiling process. A popular German type of kier for loose cotton and waste is shown in Figure 115.

10. **Kiers for Skein Yarn.**

Skein yarn may be boiled-out in open tanks or in closed kiers. In the former case round wooden tanks are used provided with a false perforated bottom. Circulation is obtained either by a central vomit pipe leading from the bottom of the tank up to the top, or by one or

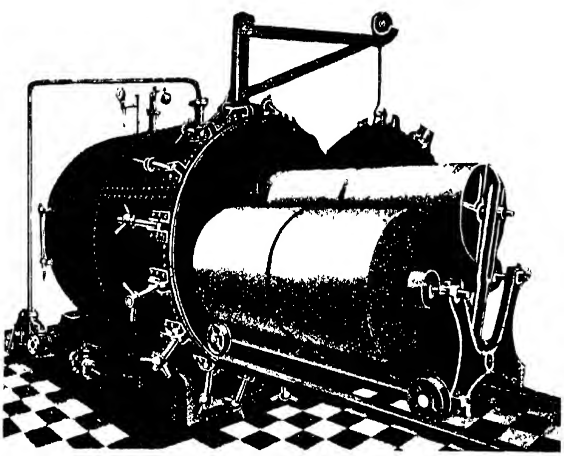

FIG. 145.—Jackson Open Width Kier.

more external side pipes into which steam may be injected at the bottom, thus carrying the liquor upward and distributing it over the goods at the top. More satisfactory boiling, however, can be obtained by the use of closed pressure kiers. These are cylindrical vessels constructed of boiler-plate iron, provided with a movable top for the introduction and removal of the goods, and are constructed in various sizes according to need from a capacity of 1000 to 10,000 lbs. of material,

The circulation of the liquor is procured by a variety of means depending on the special type and construction of the kier, as explained above.

In packing skein yarn into kiers the separate skeins are usually headed up into bundles of about two pounds weight, the method being to take this amount of skeins and then run a single skein through and fasten with a loosely tied loop. These packages of yarn are then systematically packed in the kier as uniformly as possible, overlapping the layers so as to avoid making channels. Another way of handling is to tie small bundles of the skeins together with a piece of small cotton rope so as to form a continuous chain and to run the goods in this form. Outside of the difference in handling in this manner the boiling-out of skein yarn is conducted practically in the same way as with warps or cloth. The mass of skein yarn in the kier is generally rather easily penetrated by the liquor, even more so than with cloth, though owing to the comparatively large unit packages there is more danger of channelling, especially at the sides of the kier, and along the central vomit pipe if such be present. On this account particular care should be given to the proper packing of skein yarn. Tight and bulky knots should also be avoided.

Kiers used particularly for the boiling-out of skein yarn in bundles, or other small package materials, such as hosiery, etc., generally have the top constructed somewhat differently than with kiers for cloth or chain warps. In the latter case the kier top is a fixed part of the kier itself, and the material is introduced and withdrawn through a manhole located either towards the side of the top or at the center. Kiers for boiling-out skein yarns, however, are provided with a top which is completely removable from the kier and which is held in place by strong swivel bolts. A type of kier of this character is shown in Figure 116. This particular kier is provided with a rotary pump and the liquor is circulated up through a central vomit pipe. The heating is done with a closed steam coil beneath the false bottom within the kier. The movable cover contains the blow-off and safety-valves and the pressure gauge, and there is an overhead tackle or swinging crane for lifting the cover and moving it to one side during the packing and unpacking of the kier. A small type of kier for boiling skein yarn is shown in Figure 117. This is provided with three outside injector circulators located on the sides of the kier. The top is completely removable and is lifted by means of a chain and set of gears turned by hand. Such a kier is very useful in a small bleachery.

Whatever type of kier is used, and in whatever form the cotton may be boiled-out (whether skein yarn, chain warps, or cloth), it is very essential that the material be packed into the kier in such a manner as to promote even distribution and circulation of the liquor through the cotton. In other words, the density of the material throughout the kier should be as uniform as possible. If the goods are introduced into the kier in a haphazard manner they will pack down so that some parts are closely packed while others are loosely packed, and such a condition will, of course, result in a channeling of the liquid in passing through the cotton, so that some portions will be

over-boiled and others under-boiled. Even boiling is one of the chief problems which the bleacher must deal with, and the chief factor in this problem is even packing of the goods in the kier.

When iron kiers are newly used there is always considerable rust to be met with on the sides which are liable to stain and damage the goods. This rust should be well scraped off with a wire brush, and the sides of the kier given a coat of whitewash, or better yet, a coat of cement which may be brushed on. The use of the kier with alkalies will tend to harden this coating. In the case of kiers used in lime-boiling the lime liquor will soon form a hard scale on the surface of the iron which will prevent rusting.

11. Types of Open Kiers.

The open type of kier is shown in the following Figure 114. The circulation in this case is obtained by a central vomit pipe running up through the kier and surmounted by a dome shaped spraying device which throws the liquor evenly over the entire surface of the goods. The steam is introduced at the bottom of the kier beneath the false bottom, and this forces the liquor in the well up through the vomit pipe. Such kiers are usually provided with a removable cover with a vent-pipe for the escape of the steam. When loading and unloading the kier the entire cover is removed.

Another more modern form of open kier is shown in Figure 118. In this apparatus the circulation is produced by means of a centrifugal pump, which forces the liquor through an outside tubular pre-heater and thence over the top of the goods in the kier. This kier is constructed of iron, and is recommended for use in the boiling of fabrics containing colored headings or stripes, of such character that boiling in a pressure kier would cause the color to run and stain the whites.

In open boiling care must be exercised that the goods are packed very uniformly, otherwise on account of lack of pressure in the kier the liquor will not penetrate through the fiber. Also it is necessary to avoid exposure of the fabric above the surface of the liquors during the boiling operation; on this account a latticed wooden grid is placed over the top of the material so that it is completely submerged beneath the liquor. After the boiling-out is finished and the hot liquor run off, the kier should be immediately filled with hot water to prevent any of the cotton from becoming dry before washing out the alkaline lye.

According to Trotman and Thorp the difference in the action of the injector and the puffer pipe is that the former gives a continuous circulation for a much smaller expenditure of steam, as the cones of the injector are proportioned to utilize the velocity of the steam in an efficient manner, so that the heating of the liquid is only gradually affected and requires much longer than with the puffer. The puffer really consists of a small conical chamber somewhat like an inverted flower pot, and this is fixed in the well beneath the false bottom of the kier and is provided with apertures for the inlet of liquor which has drained through the cloth into the well. A vomit pipe of 4 to 5 inches diameter rises from this cone through the center of the kier and

terminates at the top in a bonnet which acts as a spreader, the latter, of course, being situated above the line occupied by the goods in the kier. A steam nozzle, not however reduced to a small cone form, rises into the center of the puffer base, and almost up the top of this base, where it enters the vomit pipe. In order to obtain proper results with the puffer it is necessary that this height of the steam nozzle should be carefully adjusted, for it is necessary to avoid the discharge of the steam into the well rather than up into the vomit pipe. The operation of the puffer is intermittent, hence its name. The well liquor rises in the vomit pipe to a level depending on the amount of liquor in the kier; the steam discharging into this column of liquor heats and expands it until a point is reached when the steam no longer condenses, with the result that the whole column of liquor is ejected

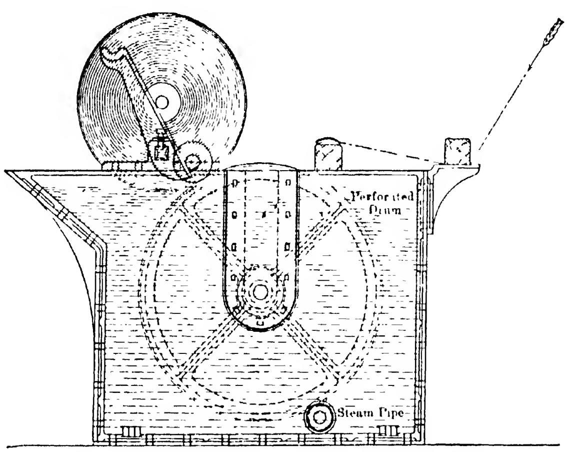

FIG. 146—Open Kier for Cloth (Butterworth).

bodily up against the spreader and thus sprayed over the top of the goods. A fresh column of relatively cool liquor immediately rises in the tube and the operation is repeated. In this so-called vomiting or mildly explosive intermittent mode of circulation of the liquor there is a sort of pumping action on the mass of the goods in the kier, with the result that the goods rise and fall in the liquor to quite some extent, this effect being more apparent with heavy cloth than with light and spongy fabrics. It is claimed that this motion of the goods causes continual changes in the contact with the liquor which makes for thorough and uniform penetration. On the other hand goods with colored headings are more liable to show a bleeding with this action than when a gentler and more continuous circulation is employed. The lifting capacity of the puffer against the pressure of the liquor in the kier is less affected by rise in temperature than is the case with the steam injector; in either case, however, there is danger of a discharge

of steam directly on the goods when the temperature of the kier liquor reaches a point near its maximum. On this account it is well to lag the vomit pipe with sacking or burlap in order to break the flow of steam. It is necessary for the operator to maintain a supervision over the flow of steam in the kier, so that if the steam pressure at the top of the kier becomes greater than the pressure of the liquor in the well, the flow of steam must be checked until equilibrium is re-established and the boiling carried on at a more moderate pace.

When either the injector or puffer system is used with an open kier, it may sometimes be found that due to lack of penetration or loss by boiling over, there may be a deficiency of liquor in the well. This is especially liable to happen at the start of the boil before the goods have become well soaked and the liquor does not drain down quickly enough. When this condition develops it is necessary for the operator to by-pass the liquor from the top of the kier through a suitable valve and pipe, or sometimes a rather primitive arrangement is resorted to such as the insertion of a stout wooden beam at one side of the kier during packing, and this is agitated to make a groove for the flow of the liquor directly down through the mass of goods. Whatever the device employed, however, it must be emphasized that steam should not be allowed to collect in the bottom well, which should be always filled with liquor.

12. Types of Pressure Kiers.

At the present time the open type of kier is very little used except in small bleaching installations, and chiefly for the boiling-out of skein yarn. Sometimes where a boiling-out is desired previous to dyeing, and not for bleaching, the open kier is still used. For most purposes of bleaching, however, the open kier has given way to the closed pressure type of kier, which operates much more efficiently and thoroughly.

In Figure 119 is shown the diagram of a pressure kier where the circulation is brought about by an injector in a central-vomit pipe. A kier of this character 9 feet deep and 6 feet in diameter will hold about 4000 lbs. of cloth and somewhat less of yarn. Another form of a similar type of kier is shown in Figure 120.

There is another type of injector which has the circulating pipe outside of the kier. The principle of its action is practically the same as the foregoing, the liquor being sucked from the bottom chamber of the kier, and forced up through the circulating pipe and sprayed over the top of the goods. Having the circulating pipe on the outside of the kier has the advantage of leaving the kier free of obstructions inside so that more goods can be introduced; and furthermore it greatly simplifies the uniform packing of the goods, as it is rather difficult to prevent channelling along an inside central vomit-pipe. An outside circulation kier is shown in Figure 121.

Another form of the outside injector type of kier is that made by Allen; this is an American built machine (see Figure 122) and was formerly quite popular, but in more recent years has given way to a similar kier provided with a pump system of circulation, and known as

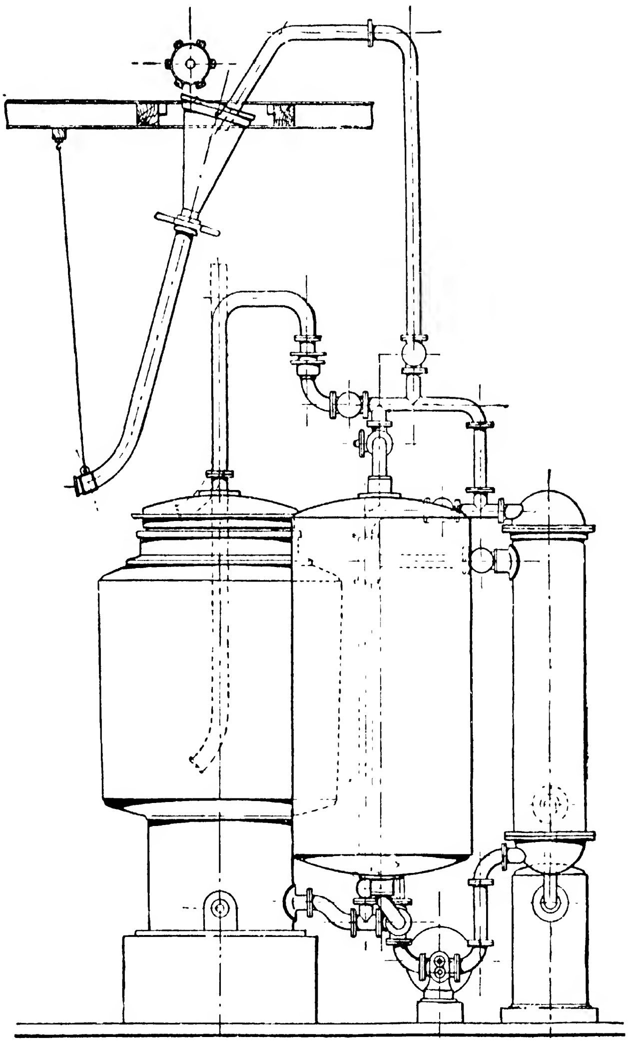

FIG. 147.—Thies Kier with Mechanical Feeder.

the Allen-Worcester kier (see Figure 131). In pump kiers the pumping apparatus should be so designed that the entire body of the liquor in the kier is circulated every 20 minutes. Owing to the fact that the liquor is not diluted with steam as in the injector type, the pump

system of kier circulation has been rapidly growing in favor among bleachers.

In the Barlow and Pendelbury kiers, which are used quite largely in England, the circulation is brought about by steam pressure alternately forcing the liquor out of the kier and then in again. In the Barlow design there are two large kiers provided and these must be run in sets of two. The goods in the first kier are boiled; and then steam is introduced which forces the liquor over into the second kier. This action alternates about every 15 minutes. These kiers are shown in Figure 124. When the kiers are first started, steam is blown into both kiers in order to expel all the air. Then boiling lye is run into the first kier until it is filled. Steam is now admitted through the central pipe, which causes pressure-boiling of the goods in the kier. After about 15 minutes the two-way valve is so adjusted that the steam is shut off and admitted to the top portion of the kier. This causes the liquor to be forced out through the goods to the pipe and then over into the second kier. The valves are then readjusted so as to boil the goods in the second kier for 15 minutes, when the liquor is again blown over into the first kier. The alternate boiling of the two kiers is continued for 4 to 6 hours to obtain a complete boil-out. In this system of boiling the goods are alternately steamed by saturation with high-pressure steam and then subjected to the action of boiling lye. Whether or not these conditions are the most desirable is a matter of doubt. This kier also requires considerable and constant attention in the regulation of the valves; furthermore, owing to the fact that they must be operated in pairs, they require a large amount of goods to fill them.

The Pendelbury kier is a modification of the Barlow system in which the second kier is replaced by a smaller reservoir into which the liquor can be alternately forced and withdrawn (see Figure 125). With this exception the principle of the action is the same.

The more modern type of kier is automatic in its operation; the liquor being regularly circulated by means of some automatically controlled device or by means of a pump. The pump circulation is well illustrated in the Walsh kier (see Figure 126). In this kier the liquor is drawn from the bottom chamber by means of the centrifugal pump and circulated through the tubular heater, and thence forced again into the kier at the top. This type of kier is said to be particularly adapted to the caustic soda boil since live steam does not come in contact with the boiling liquor. The boil-out is usually carried on at a pressure of 25 to 50 lbs. per sq. in. and for 4 to 8 hours, depending on the nature of the goods. This kier is usually provided with two manholes and the cloth in rope form is run into the kier in two strings, one through each manhole. The speed of filling (and also of emptying) is about 200 yards per minute.

One engineering objection to the pump method of circulation is in the heat losses incurred in the outside circulation of the liquor and the rather low economy of transferring the force of the steam through secondary driving mechanisms. By covering the pipes, however, with

efficient insulating material it is possible to cut these heat losses down to a low point.

The Jefferson kier uses an automatic device for the circulation of the liquor, and is being largely used in both America and England. The kier shell is similar to any ordinary form and is made in various sizes capable of holding from 1000 to 9000 lbs. of goods. The circulating device consists of a receiver which is located alongside of the kier proper. The circulation is based on an alternate application of vacuum and steam pressure. The working of this kier can be understood by reference to Figure 127. After the kier is packed with the goods and filled with liquor, the latter drains through the effluent pipe (1) and check-valve (K) into the receiver (R); it also rises through the side-pipe (2) and into the hollow ball (B). This ball, together with its connected parts, oscillates through a small angle on the pivot (V) and is counterbalanced by the weight (W). When the ball becomes filled with liquor its weight overbalances that of the counterpoise (W), with the result that it moves down through a small angle and opens the steam valve (3). High pressure steam then passes into the receiver and forces out the liquor through the pipe (4) and the check-valve (5) into the top of the kier.

As the steam is now shut off from the receiver, the residue therein condenses, resulting in a partial vacuum. This condition causes a fresh quantity of liquor to be drawn over by suction from the bottom of the kier, and the receiver and ball once again become filled with liquor and the cycle of operations start again. When the kier is first started the injector from steam-pipe (8) heats up the circulating liquor, and at the same time aids in the circulation, and indeed when the liquor is cold this injector first starts the circulation, and when it ceases its action the receiver automatically takes up the operation. In the operation of the Jefferson kier it is essential that the steam pressure at valve (10) should be sufficient to overcome the pressure in the kier together with the head and friction encountered in forcing the liquor from the receiver. The initial steam pressure should be at least 65 lbs. per sq. in. The need of high steam pressure and the complicated valves employed are the chief objections to this kier. Otherwise it gives a very efficient and positive circulation with an automatic control, which highly recommends it. The intermittent discharge of liquor causes the goods to rise and fall in the kier with beneficial results in boiling-out. The consumption of steam in this kier is also relatively very small, and owing to the thoroughness of the circulation it requires less time and weaker solutions of alkali to effect the boiling than with most other kiers.

A trouble which is sometimes experienced in kier-boiling is that of the turning over of the goods in the kier, causing great tangling and confusion when the goods are run out of the kier. This trouble may be due to two causes: (a) improper packing of the goods in the kier so as to allow of uneven pressure developing in the mass of the material, or (b) improper control of the circulation whereby a partial vacuum is produced in the upper part of the kier, causing the goods to be lifted

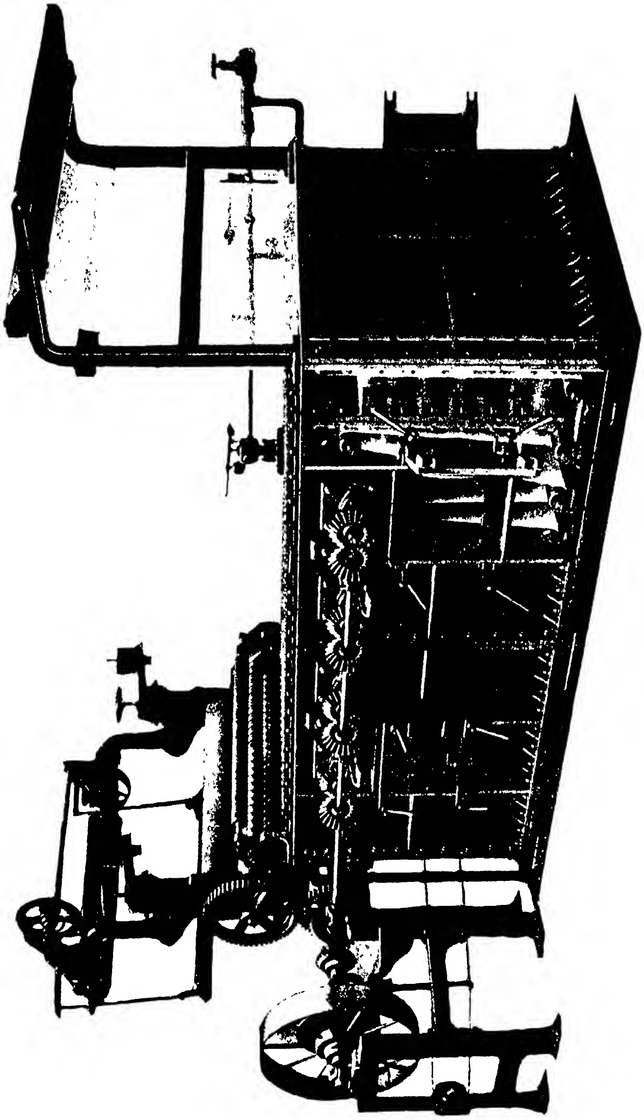

FIG. 148.—Bentz Open Width Kier.

up and rolled over. This condition may sometimes arise by accident, as when cold water is admitted at the top of the kier during its operation. This will cause rapid condensation of the steam in the vacant space above the goods and produce a vacuum. Or sometimes at the end of the boil cold water is admitted at the top for washing purposes, and if this is not done carefully the same condition of a vacuum may arise.

In closed or pressure kiers the top of the goods should be covered with a stout cloth and held down in place by chains attached to the side of the kier. This is quite important as a practical precaution, for if the top of the goods is left free there is danger that some portion may be projected against the safety-valve outlet so that the internal pressure may rise beyond the proper point and even lead to an explosion of the kier. The top of the goods should also be held in place to prevent tangling and overturning due to rise of the whole mass by pressure from beneath. A good precaution to take in the construction of the kier is to have the outlets of the safety-valve and air-valve protected by a sturdy perforated bonnet.

A rather popular type of kier in Germany and Europe is one in which the circulation is conducted horizontally through the kier rather than vertically from top to bottom. The apparatus is generally known as the Gebauer kier and is characterized by consisting of two concentric vessels, the one within the other, and the inner one with perforated walls. The kier also contains a central vomit pipe which is perforated almost its entire length. The circulation may be brought about by an internal injector at the base of the vomit pipe or by means of an outside pump. An outside tubular heater is also provided. The liquor is forced up through the central vomit pipe and circulates out horizontally through the goods and thence passes back through the perforations of inner container to the bottom well. This type of kier is also known as the "sectional" kier. The general construction and method of operation of this type of kier may be readily understood by reference to Figures 133 and 134.

13. Steam in Kier Heating.

The relation between steam temperature and its heating value as far as kier boiling is concerned is stated very lucidly by Trotman and Thorp[13] as follows: When water is heated at atmospheric pressure, it rises to a temperature of about 100° C. (212° F.), at which temperature boiling takes place without further rise of temperature, although additional heat be applied. This additional heat is not, however, lost, but does internal work in the nature of effecting mutual repulsions between the molecules of water, and when a definite amount of heat has been absorbed, the water changes its physical condition into that of steam. Thus taking as a unit the amount of heat which under normal atmospheric conditions, raises 1 gram of water from 0° C. to 1° C., it will be found that 537 units of heat are required to convert each gram of water at 100° C. into steam at the same temperature. But if the water be enclosed in a vessel with a safety-valve set to blow off at a

[13] *Bleaching and Finishing of Cotton Goods*, p. 140.

pressure of, say, 2 atmospheres, the temperatures at which boiling can be maintained and steam liberated will be nearly 120° C., and the additional heat that must be applied when this boiling temperature is reached in order to convert each gram of water into steam at the same temperature is 523 units, and the total heat units stored up in a gram of steam in the two cases are 637 and 643 respectively. Now the object of heating the liquor in a kier is not to convert it into steam, but to raise the liquor, which is the vehicle by means of which the drugs and heat are applied to the goods, to a temperature at which the impurities are most energetically attacked. In the application of live steam for heating purposes, the higher the pressure the greater is the heat contained in a given weight of steam, and the greater also its temperature. Also when live steam is used for heating and circulating in closed kiers, it is essential that the pressure of the steam supply shall exceed that in the kier, otherwise the liquor in the kier will cease to circulate until it has cooled to a temperature below that of the steam.

It has been observed that the heat contents of the steam consist not only of the units of heat put into the water to elevate its temperature to that of the boiling point, but also of an amount which was expended in doing the internal work of vaporization. This quantity, known as the latent heat of vaporization, is stored up in the steam and delivered to the liquor during condensation.

14. Special Forms of Kiers.

Besides the more usual type of kier for boiling-out, there have also been developed special forms of apparatus which differ quite radically in many features from the ordinary circulation kier. Some of these are particularly constructed with the idea of treating cloth in the open-width form rather than in the rope form, or the special kier may be but one part of a complete bleaching system operating under newly developed mechanical principles.

The Mather & Platt kier is a well-known apparatus of this special type. The principles of its construction and operation are unique. It may be said to consist essentially of a horizontal closed pressure boiler or container for the goods which are packed in separate receptacles and not into the kier itself. Reference to the illustrations shown in Figures 142 and 143 will make clear the general operation of this machine. It may be employed for either goods in the rope form or in the open-width; in the former case the cotton material is packed in trucks or wagons with perforated bottoms. These are run on a rail into the kier and the door is closed. This door consists of a heavy wedge shaped piece of special construction so as to insure a tight fit. The liquor is heated in an outside boiler and is circulated by means of a centrifugal pump and enters the kier through spray pipes situated over the trucks. Before the goods are placed in the trucks they are usually saturated with the alkaline solution to be employed in boiling-out. The kier within is also provided with open steam pipes for direct heating and with closed steam coils for indirect heating; the liquor may also be circulated in either direction as required. Also a vacuum may be put

on the kier at the start to eliminate all the air. After boiling-out has been completed the goods are washed in the kier by the circulation of hot water. The Mather & Platt kier may also be used for boiling-out cloth in the open width, in which case a special set of carrier rolls is used in place of the trucks and the goods are rolled back and forth within the kier, and in this manner the cloth is exposed to the alkaline treatment.

Another special form of kier is that of Thies-Herzig, which, however, is used in connection with a complete system of bleaching and is more linked up with a special process and can therefore hardly be considered from the point of view of an individual kier treatment. The kier itself is very similar to any modern type of such apparatus, but is provided with a special form of impregnating and plaiting apparatus. The characteristic of the Thies-Herzig system is a preliminary treatment of the material with an acid solution which is used warm. After washing the goods are impregnated with the lye and run into the kier through a telescopic plaiting apparatus (see Figure 147). This plaiter consists essentially of an upper funnel-shaped receiver suspended from above in a universal swivel joint; the cloth in rope form enters the funnel and passes down through the tube, which is jointed so that the parts slide into each other like a telescope, which permits of its being let down into or drawn up from the kier as desired. The universal swivel is suspended in such a manner as to allow of an oscillating movement in any direction. The material passes over a drum and is washed into the hopper or funnel with a flow of liquor supplied by a pump. The mechanical and automatic plaiting is said to give a very uniform and compact packing of the goods and also saves considerable labor. This mechanical plaiter may be used with other kiers or vats independent of the Thies-Herzig system. The Thies kier system includes the kier proper, two auxiliary boilers for the purpose of alternately withdrawing the air and receiving the lye from the kier, and also a superheater for the lye. When the kier has been filled with the goods the boil-out liquor is forced in at the bottom until the kier is quite full, the air escaping through an escape valve at the top. By pumping the liquor from the auxiliary boiler into the kier a vacuum equal to about 10 lbs. is produced in the former vessel. By proper connection with the top of the kier this vacuum takes off any residual air from the kier and also starts the circulation of the liquor as the kiers fills up. By regulating suitable valves the pressure in the kier is now increased to about 45 lbs., the superheater is brought into operation and the boiling is continued for several hours at the pressure of 45 lbs. In this system of kier boiling it is claimed that the alkali is used at a higher degree of concentration than in other systems and hence a smaller amount of liquor and steam is required.

Another special form of kier is that of Jackson (manufactured in this country by H. W. Butterworth). It is particularly designed for boiling-out in the open width, and the cloth for this purpose is first batched up in a special saturating apparatus on two rollers set in a frame. Then the frame with the rolled cloth is run into the kier and

the treatment takes place in a manner very similar to that of the Mather & Platt kier (see Figures 145 and 146). The kier stands of course in a horizontal position and the liquor is circulated by means of a pump. The movement of the cloth back and forth on the rollers is regulated in an automatic manner. In the open width system of boiling out it is claimed that a much more uniform treatment is obtained; also with cloth containing selvedges there is avoided the tendency to curl which often takes place when the cloth is run in the rope form and which frequently leads to much trouble. Of course a better width is left to the cloth and a less degree of shrinkage in length which makes the cloth fuller and less distorted.

Another form of special kier is that employed in the Edmeston-Bentz system. In this kier the goods are not packed at ail, but the cloth is run through a closed tank over sets of rollers either in the rope form or in open width (see Figures 148 and 249). In this way the cloth is brought into contact with the boiling liquor and is then given a brief contact with live steam. Warps in the rope form may also be treated in this kier in a similar manner to cloth. The material enters and leaves the apparatus through liquid seals and therefore only a moderate pressure can be obtained within the kier tank. Depending on the weight of the cloth the rate of passage through the kier varies from 30 to 45 yards per minute.

Somewhat the same idea has been applied to a continuous method of boiling-out and bleaching cloth or warps, the goods being run slowly through a series of tanks in the which the different operations are carried out *in seriatum*. By such a system, however, a very thorough boiling-out cannot be given as the goods cannot be left in the liquor but for a comparatively short time and the boiling cannot be conducted under pressure. Some compensation, however, is had for these limitations in that the cloth or warps are in the open form and are very intimately in contact with the liquor, and also stronger solutions may be used.

Another form of continuous kier is that of Rigamonti and Tagliani (see Figure 251). The cloth passes down a high column of liquor into the kier where guide rollers and appliances are so arranged that there is considerable accumulation of cloth in the kier; the cloth then leaves the kier through the same column of liquor by which it entered. This kier is used in connection with a complete bleaching system for the continuous handling of the goods from start to finish. A kier also connected with a complete system of continuous bleaching is that of Muntadas y Rovira. and its method of operation is based somewhat on the same ideas of the preceding apparatus (see Figure 237), although the goods are run through a consecutive series of chambers in the form of a long range of closed vats having a series of water seals at the two ends so that considerable pressure may be obtained in the intervening vats where the boiling-out actually takes place.

Chapter XVI.

The Bleaching of Cotton.

1. General Theory of Cotton Bleaching.

The bleaching of cotton involves two general steps in procedure; first, a removal of the fatty and waxy matters on the fiber, and second, a destruction or removal of the coloring matter. The order of these steps may not be reversed, for if the waxy matters are not first removed these will protect the coloring matter from the proper action of the bleaching agents. The bleaching of cotton involves the use of boiling alkaline solutions, sours or acid solutions, solutions of hypochlorites, and copious washing with plenty of water for the removal of all chemical residues. The nature of the boiling-out operation with alkalies has been very thoroughly investigated and has been discussed at length in the preceding pages. The decolorization, or bleaching proper, although an individual process by itself, is nevertheless dependent for its success on a careful preparation of the cotton by the previous boiling-out. Where this is imperfect or improperly conducted the action of the bleaching agents will be more or less nullified.

There are, however, certain cases of bleaching where the boiling-out process is omitted entirely and the material is bleached altogether by the action of hypochlorites or other bleaching agents; this may be done for the purpose of avoiding the loss in weight due to boiling-out or to economize the time of bleaching.

There is still considerable doubt as to the nature and identity of the coloring matter existing in the cotton fiber. It is probably a complex substance made up of several individual chemical compounds. It is, however, rather easily and completely decolorized or destroyed by the action of strong oxidizing compounds, and particularly by solutions of hypochlorites. It is fortunate in this connection that the bleaching may be effected with solutions of such dilution that the cellulose of the fiber is not attacked to any appreciable extent, provided the process is conducted with care and skill. While other oxidizing agents may also be employed rather effectively for the bleaching of cotton, nevertheless, the use of hypochlorite is favored by reason of its cheapness, efficiency, and lack of injury to the fiber.

The use of sours (dilute acid solutions) in the bleaching of cotton is always for the purpose of removing objectionable residues of chemicals by neutralization or through the formation of inert compounds that are easily removed. Sours function in two ways in cotton bleaching; first, in cleaning the fiber from lime compounds after a boil-out with caustic lime; and second, for the decomposition and removal of

chlorine compounds after the treatment or "chemicking" with bleaching powder or other forms of hypochlorite. For a sour it is only permissible to use a very dilute acid (sulfuric or hydrochloric) solution, the temperature of which also must not be too high (not over 80 to 100° F.). If the sour is not employed with caution there will be great danger of serious injury to the goods, as cotton is very easily affected by the action of acids.

Washing is a very important process in cotton bleaching, and it should never be neglected in any part of the process, if satisfactory and uniform results are to be looked for. Plenty of water must be used in all washing operations, and good clean water at that. Many defects in bleaching may be eventually traced back to the use of poor water. The whole idea in bleaching cotton is really to produce a practically chemically pure cellulose from the raw impure fiber, and this cannot be realized if the water employed in bleaching is not itself as pure as possible, for the cotton is quite absorbent (especially after passing through the chemical operations of bleaching) and will take up from the water in which it is steeped many of the impurities dissolved therein.

Since the bleaching of cotton (and of the vegetable fibers in general) is the result of a comparatively strong oxidizing action, it is an interesting question as to whether the bleaching only deals with the oxidation of the actual coloring matter, or if it extends to an oxidation of the entire substance of the fiber. Cross and Bevan[1] are of the opinion that the latter is the case and claim experimental proof of the fact. As the oxidation of the fiber substance is a variable factor depending on the rapidity of the reaction and the activity of the oxygen in the bleaching medium, there may be a considerable variation in the actual consumption of oxygen in the bleaching process. As cellulose is a molecule (or aggregation of molecules) containing aldehydic (CH.O) functions, its oxidation may result in a condensation involving either a hydrolysis or an elimination of water, according to the condition under which the oxidation takes place. Rapidity of oxidation seems to favor a minimum consumption of bleaching oxygen, and the rapidity of the reaction is determined by the presence of highly active oxygen. When compared with solutions of bleaching powder, Cross and Bevan are of the opinion that electrolytic bleaching liquors present the best conditions for the smallest consumption of oxygen, as in such liquors the oxygen exists in a very active condition.

The bleaching agents employed for cotton and the vegetable fibers in general are all oxidizing agents. Reducing agents do not appear to have very much effect on the natural coloring matters of cotton and consequently are not applicable to this character of bleaching. A good many years ago Koechlin and Saget proposed the use of calcium bisulfite (which is a reducing agent) for the bleaching of cotton; but the results obtained were evidently not of sufficient value to give it any standing in practice. According to this process, cotton cloth, for example, was impregnated with a solution consisting of 1 liter of water, 100 gms. of lime, and 500 gms. of sodium bisulfite (40° Bé.), then

[1] *Jour. Soc. Chem. Ind.*, 1887, p. 172.

steamed for 1 to 2 hours under 1 to 2 atmos. pressure or boiled for several hours, and finally washed, soured and washed again.

Of the oxidizing agents employed as bleaching materials for cotton the most important are the compounds of hypochlorous acid (calcium hypochlorite and sodium hypochlorite); next in importance are hydrogen peroxide and sodium peroxide, or other peroxide salts which yield hydrogen peroxide when brought into solution; and finally potassium or sodium permanganate. Other compounds capable of liberating "active" oxygen are not of any practical importance in the bleaching of cotton, either because the price of the chemicals is too high or because their use is dangerous to the strength or quality of the fiber. For instance, it has been suggested to use nitric acid or *aqua regia* (a mixture of nitric and hydrochloric acids), as in the French patent of Delescluse; also nitrous acid, as in Tabary's process.[2] These chemicals

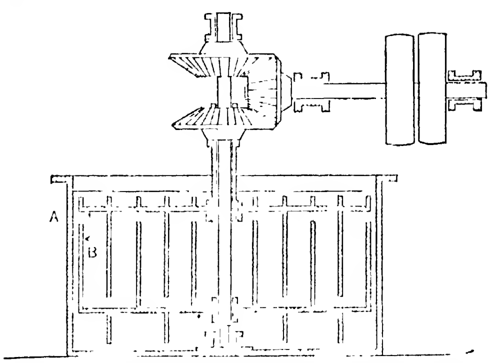

FIG. 149.—Grinding Machine for Chloride of Lime.

without doubt exhibit strong bleaching properties with respect to the coloring matters of cotton, but at the same time their use is so dangerous to the fiber that the processes employing them are of no practical value. Rather unusual bleaching methods have also been suggested, as, for instance, the "patented" process of Jardin for the use of nitrous acid, the latter being made by the action of molasses on nitric acid. Also the method of Bonneville,[3] where nitric acid vapor is allowed to act on cotton cloth impregnated with sugar. These processes are not only absurdly dangerous to the fabrics but are also dangerous to the workmen, owing to the very poisonous quality of the vapors of nitrous acid.

2. Chlorine Bleach Liquors.

While the bleaching of cotton is very generally spoken of as "chloring" the expression is not quite a proper one, as the bleaching action is not that of chlorine itself but of solutions of salts of hypochlorous

[2] *Ger. Pat.* 101,285.
[3] *Ger. Pat.* 16,036.

acid. The fact, however, that in the use of these hypochlorite solutions (either of bleaching powder or sodium hypochlorite) the odor and irritating effects of chlorine vapors are quite noticeable, has caused the workmen in the bleach-house to refer to the operation as "chloring." The rather prevalent use at the present time of chlorine itself in the liquefied form for the preparation of the hypochlorite liquors, perhaps, gives this term now a more truthful meaning than could be ascribed to it formerly. The most apparent odor from bleach liquors is really that of hypochlorous acid and not that of chlorine itself. This is particularly noticed when the cotton goods are impregnated with the bleach liquor and then folded down in trucks or bins to oxidize; also when the goods are run into a "sour" or acid bath after treatment with bleach liquors. Chlorine is at times noticeable in the bleach house when chloride of lime is used and the powder is exposed to the air, or when particles of the undissolved chloride of lime come in contact with acid.

The action of chlorine bleach liquors is based on their content of "active" chlorine, which is to say, on the amount of hypochlorous acid (or its salts) which is present; since it is from the hypochlorous acid that the oxygen is derived and effects the oxidation and decomposition of the coloring matter. During bleaching the fiber is not chlorinated at all, or at most to a very slight degree. This chlorination only takes place with the impurities in the cellulose, such as albumin and lignin.

3. Efficiency of Bleach Liquors.

Though the total bleaching possibility of a hypochlorite solution depends, of course, on the total amount of "active" chlorine present, nevertheless, the energy or strength of the bleaching appears to depend on the ease or rapidity with which free hypochlorous acid is liberated. A solution of chloride of lime, for example, contains a hypochlorite salt which is rather stable and does not tend to produce free hypochlorous acid very rapidly; whereas a sodium hypochlorite solution prepared from chlorine gas and soda ash tends to free the hypochlorous acid more rapidly and consequently its bleaching energy or bleaching "efficiency" is considerably greater for an equal content of active chlorine. The same thing is true of hypochlorite solutions prepared electrolytically. Foerster and Jorre state that the rapidity of decomposition in the case of hypochlorite solutions having the same concentration is proportional to the square of the amount of free hypochlorous acid present in the solution, and with the same acid content is proportional to the hypochlorite concentration. It must be remembered that the bleaching oxygen originates from the free hypochlorous acid and not from its salts (sodium hypochlorite or calcium hypochlorite). From this point of view Kind is of the opinion that there may be some structural difference between the salts and the free hypochlorous acid, supposing that in the case of the salt the formula is $Na — O — Cl$, whereas in the case of the free acid the formula is $H — Cl = O$, in the latter case giving the chlorine a valence of three. This is said to be further supported by the fact that free hypochlorous acid, similar to carbonic acid, when in aqueous solution is present chiefly as the

anhydride, and this as is well known has an especially vigorous oxidizing action. This reaction involving the consideration of the free hypochlorous acid as a measure of the bleaching energy or bleaching efficiency of the liquor, is of the utmost importance in the discussion of the bleaching process.[4]

Free hypochlorous acid may occur in bleach liquors through several causes: (a) by dissociation or hydrolysis of the hypochlorite salt, (b) by decomposition through the action of a stronger acid, or (c) it may be spontaneously present as in an electrolytic hypochlorite liquor. The hydrolytic action is very small; a normal "neutral" sodium hypochlorite solution containing 52.5 grams of sodium hypochlorite per liter, as a result of hydrolysis alone contains only 3.5×10^{-4} molecules, or 0.0018 percent of hypochlorous acid. The hydrolysis, however, rises rapidly with the temperature.[5] This accounts for the fact that a bleaching liquor having an excess of caustic soda present shows a much lower bleaching efficiency than a solution which is more nearly neutral.

The loss in hypochlorite strength of a bleach liquor depends, in the first place, on the relative amount of free hypochlorous acid originally present. The following table by Foerster and Abel shows the time required for a 10 percent loss in strength:

Percent of free hypochlorous acid	Time in minutes required for loss of 10 percent in strength
0.11	261.0
0.293	34.6
0.65	6.8
1.02	2.8
1.37	1.6

If the solution be made neutral by the addition of caustic soda solution the free hypochlorous acid content decreases about 30 times, and consequently the stability of the solution increases about 900 times.

4. Control of Bleaching Velocity.

It is possible by the addition of soda ash or caustic soda to control the spontaneous decomposition and bleaching effect of the chemic solution. According to Nussbaum and Ebert, it is possible by this means to almost completely neutralize the free hypochlorous acid. Kind and

[4] In former times bleachers were accustomed to render their chemic solutions more active by slight additions of sulfuric or hydrochloric acid. It may readily be understood that the free hypochlorous acid possesses a greater bleaching power if there is added a larger quantity of acid than is necessary for the neutralization of the free alkali present. Since, however, the alkalinity varies it does not always follow that an equal addition of acid corresponds to an equal rise in the bleaching efficiency. It is also easy to make the bath too acid and thus increase its bleaching energy to such a point that there is danger of injuring the fiber. On strongly acidifying the solution free chlorine is also developed:

$$HOCl + HCl = H_2O + Cl_2$$

As the addition of mineral acids, as a rule, causes bad results in bleaching it has become customary to use the milder organic acids such as acetic or formic acid, or even carbonic acid.

Lunge (*Ger. Pat.* 31,741 of 1884) recommends the use of acetic acid as an addition to the bleaching bath. The hydrochloric acid resulting from the decomposition of the hypochlorous acid during bleaching is thus neutralized by the calcium acetate (formed by the interaction of the acetic acid and the lime) and free acetic acid is liberated once more. In this manner the bad effects due to the presence of the hydrochloric acid are avoided. It does not appear, however, that this process has been generally adopted by bleachers, and it is probable that the effects due to the hydrochloric acid have either been overestimated or not properly understood.

[5] Abel, *Theorie der Hypochlorite.*

Weindel, however, in comparing the effect of soda ash and caustic soda in this respect find that the latter is much better for the purpose of regulating the stability of the solution. With regard to the use of sodium bicarbonate as an addition to bleach liquors of sodium hypochlorite it has been shown by Nussbaum and Ebert that such addition is valueless for stabilizing. The addition of the bicarbonate, however,

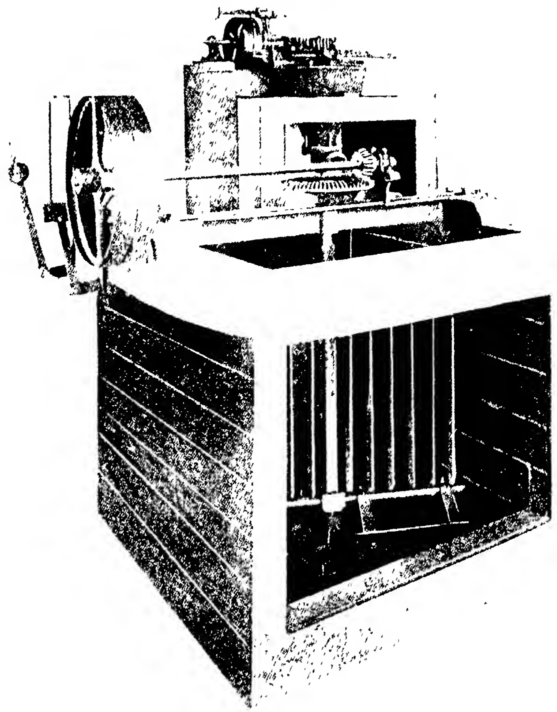

FIG. 150.—Mill for Preparing Chemic Solutions.

would have the effect of combining with any free chlorine that might be present in the solution, and in some cases this action may be of benefit as the presence of free chlorine is not desirable owing to its detrimental effect on the fiber. The reaction in this case is as follows:

$$Cl_2 + NaHCO_3 + H_2O = HOCl + NaCl + H_2CO_3.$$

In the presence of relatively large amounts of alkaline earth salts (lime or magnesium) in the hypochlorite solution the addition of so-

dium bicarbonate sets free some hypochlorous acid and precipitates calcium carbonate:

$$Ca(OCl)_2 + NaHCO_3 = CaCO_3 + NaOCl + HOCl.$$

The bleaching velocity of solutions containing the same amounts of active chlorine is dependent on the starting reaction that regulates the liberation of free hypochlorous acid. Kind and Weindel have made quite elaborate experiments on this question, and as it is difficult to accurately test the progress of the bleaching on white cloth they used standard samples of indigo-dyed yarn. Lunge and Landolt also did somewhat similar work on the bleaching energy of hypochlorite solu-

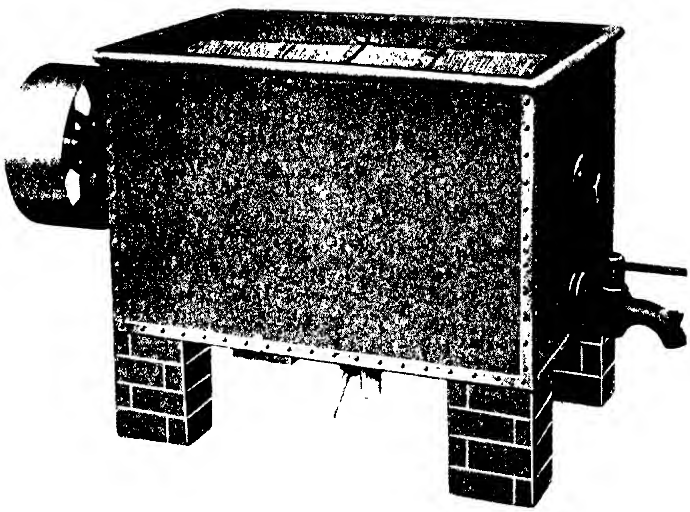

FIG. 151.—Apparatus for Dissolving Bleaching Powder.

tions by using cloth dyed with Turkey-red. Bleach liquors containing varying amounts of caustic soda or hydrochloric acid were used. In the bleaching of the indigo samples the results probably do not exactly show a definite relation to that of bleaching undyed cotton, since the indigo is very rapidly destroyed in an acid bath of hypochlorite. Kind and Weindel also made tests for bleaching velocity, using undyed cotton yarn and observing the time required to obtain the same degree of whiteness. The results have only a comparative value without any great degree of accuracy on account of the fact that it is very difficult to obtain a sharp "end point" for the bleaching, and furthermore since the appearance of the white color on the sample suffers a change on washing and drying, this being especially true when acid bleach liquors are used. The following table gives a record of the tests:

BLEACHING TESTS OF EGYPTIAN YARN USING 600 C.C. LIQUOR AT 18° C.

	Hr.	Min.
(1) Without addition	1	
(2) With 0.3 gm. caustic soda	4	45
(3) With 0.06 gm. caustic soda	1	27
(4) With 0.03 gm. caustic soda	1	22
(5) With 0.006 gm. caustic soda	1	6
(6) With 0.003 gm. caustic soda	1	4
(7) With 0.5 gm. hydrochloric acid (20%)	0	53
(8) With 2.5 gm. hydrochloric acid (20%)	0	44

5. Effect of Carbonic Acid.

One of the most important reactions influencing the velocity and progress of the action of chloride of lime solutions in bleaching is that of carbonic acid of the air. The following formulas show the progress of this reaction:

$$Ca(OCl)_2 + H_2CO_3 = CaCO_3 + 2\ HOCl, \text{ and}$$
$$NaOCl + H_2CO_3 = NaHCO_3 + HOCl.$$

That is to say the carbonic acid of the air sets free hypochlorous acid, and in the case of bleaching powder forms carbonate of lime, while in the case of sodium hypochlorite (according to investigations of Siemens and Halske), bicarbonate of soda is formed. The free hypochlorous acid spilts off the active bleaching oxygen, forming at the same time some hydrochloric acid, which either reacts with a further quantity of hypochlorite or decomposes the carbonate or bicarbonate to form free carbonic acid, which again takes part in the reaction as before. The reaction between carbonic acid and sodium hypochlorite is never complete, in that it is always a reversible reaction, depending on the relative amounts of the two substances present for its exact equilibrium.

As the action of bleaching agents on the organic impurities in the cotton fiber is an oxidizing one, the chief resulting product is probably carbonic acid, and this latter, no doubt, also enters into the reaction in its effect on the bleach liquor and so influences somewhat the velocity of the bleaching. As the bleaching progresses the relative proportion of carbonic acid entering into the process without doubt increases, with the result that the alkalinity of the solution suffers a readjustment with a consequent change in the hypochlorous acid concentration, and this of course increases the velocity of the bleaching reaction. This no doubt accounts for the fact that in practice an old bleach liquor, though naturally somewhat weaker than a freshly prepared one, gives a quicker bleaching than a fresh liquor, provided, of course, that the liquor still contains a sufficient amount of active chlorine. To substantiate this point of view Kind has made some tests using a bath of 60 liters of chloride of lime and 5 kilos. of Egyptian yarn, testing progressively the active chlorine content and the acidity of the bath in terms of hypochlorous acid in grams per liter:

		Active chlorine Gms. per liter.	Acidity HOCl Gms. per liter.
(1)	Concentration at start	2.77	— 0.341 (alk.)
	after 10 minutes	2.40	— 0.273 "
	after 20 minutes	2.13	— 0.220 "
	after 30 minutes	1.99	— 0.168 "
	after 40 minutes	1.86	— 0.147 "
(2)	After using 3 times	1.69	— 0.063 "
	after 10 minutes	1.28	— 0.018 "
	after 20 minutes	1.06	— 0.005 "
	after 30 minutes	0.92	+ 0.042 (acid)
	after 40 minutes	0.85	+ 0.110 "

In the second set, although a weaker chlorine solution was employed, the bleached white obtained after 20 minutes was considerably better than the corresponding test in the first set.

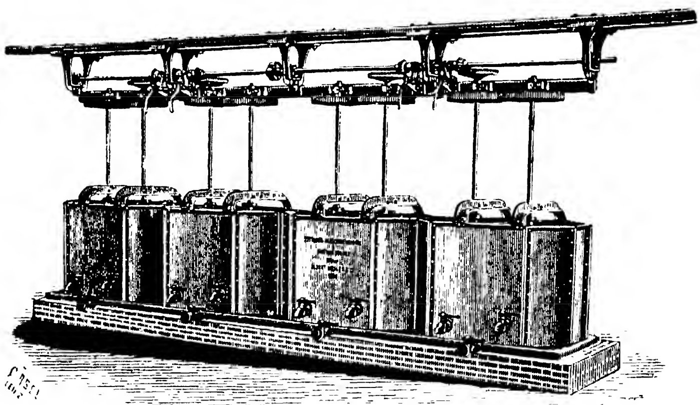

Fig. 152.—Bank of Chemic Solution Tanks.

In practical bleaching it is doubtful if the usual operator in the mill has any clear conception of the importance of the effect of the carbon dioxide on the progress and rapidity of the bleaching process, or if he takes it sufficiently into account in the regulation of his methods. If the cotton goods after being saturated with chemic liquor are exposed for some time to the air, or as in the case of skein yarn or warps, the materials are worked in the liquor so as to come into contact with the air, this effect of the carbonic acid will be very apparent. As the air, however, contains only a minute quantity of carbon dioxide, processes for increasing the bleaching effect have been devised in which the chemicked goods are treated directly with carbon dioxide gas. Thompson and Rickman[6] describe a process of this order for the bleaching of cloth. Lagache[7] also describes a process for increasing

[6] *Ger. Pats.* 26,839 and 30,830.
[7] *Deutsche Farber-Zeit.*, 1902, p. 313.

the bleaching effect and regulating the process by introducing carbonic acid gas directly into the fresh bleaching powder solution, this idea being based on his observation that the use of old bleach liquors resulted in an economy of chlorine consumption, and that the baths become more and more acid in reaction. These methods, however, have never been adopted commercially, as it is questionable if the bleaching takes place with sufficient regularity. On the other hand the activating carbon dioxide does play a rôle where old bleach liquors are continually used with suitable additions of fresh stock chemic solution. This advantageous use of old baths is especially recognized in linen bleaching, where it is generally considered necessary first to "work" the bath with some old material before the chemic gets into proper condition for use. Since the bleaching energy of old baths, however, is not at all a constant one and as successive use of the bath brings into the liquor a gradually increasing amount of impurities, the too long-continued use of old bleach baths becomes of questionable value. It is doubtful if any bleach bath should be run for a longer period than one week.

6. Effect of Salts on Bleach Liquors.

In old chloride of lime solutions and in sodium hypochlorite liquors large amounts of neutral salts are present, and this is also especially true of electrolytic hypochlorite solutions which contain a high proportion of common salt. It is interesting, therefore, to investigate the effect of these salts on the bleaching activity of the solutions. Where a large amount of neutral salts are present the solution must possess a lowered degree of diffusibility, and consequently must take a longer time to penetrate and bleach the fiber. Experiments have shown, however, that the addition of salt increases the velocity of decomposition of the hypochlorite; therefore, the effect of decreased diffusibility is offset and it is probable that the presence of neutral salts such as common salt and calcium chloride has but little practical effect on the bleaching process. The presence of substances capable of acting in a catalytic manner, however, is of more importance. It is well known, for instance, that very small quantities of cobalt compounds have an energetic decomposing action on hypochlorite salts; so much so, in fact, that these catalyzers are used in the laboratory in a practical manner for the preparation of oxygen gas by warming with hypochlorite solutions. Abel has shown that in the preparation of electrolytic hypochlorite liquor the presence of even small amounts of catalytic impurities (such as the oxides or salts of metals like nickel, cobalt, iron or copper) causes the rapid decomposition of the solution. Many of the rather obscure irregularities noticed in bleacheries are often due no doubt to the reactions taking place through the influence of catalytic agents. White [8] has found that tender spots developed in the bleaching of linen cloth were caused by the presence of small specks of iron oxide (rust). At such points the hypochlorite is acted on with great vigor so that excessive oxidation takes place and weakness is developed through the formation of oxycellulose. He found that the presence of salts of

[8] *Jour. Soc. Chem. Ind.*, 1903, p. 132.

		Active chlorine Gms. per liter.	Acidity HOCl Gms. per liter.
(1)	Concentration at start	2.77	— 0.341 (alk.)
	after 10 minutes	2.40	— 0.273 "
	after 20 minutes	2.13	— 0.220 "
	after 30 minutes	1.99	— 0.168 "
	after 40 minutes	1.86	— 0.147 "
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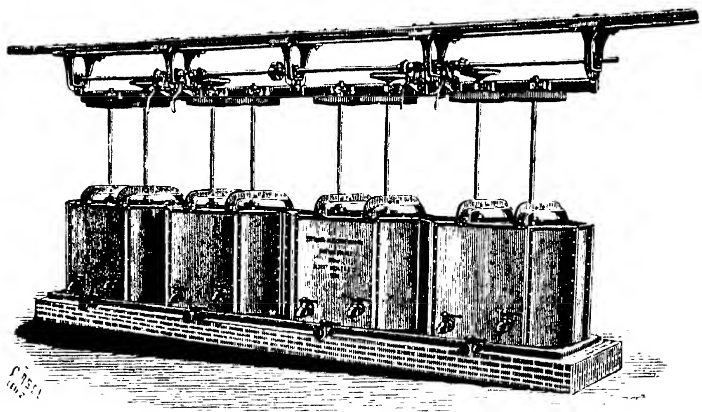

FIG. 152.—Bank of Chemic Solution Tanks.

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[6] *Ger. Pats.* 26,839 and 30,830.
[7] *Deutsche Farber-Zeit.*, 1902, p. 313.

known by the name of "Javelle water." The next advance in the matter of chlorine bleaching was the discovery in 1798 by Tennant, an English chemist, that chlorine would readily combine with slaked lime to form a good bleaching compound and one which was much cheaper than that of Javel. Tennant prepared his compound by passing chlor-

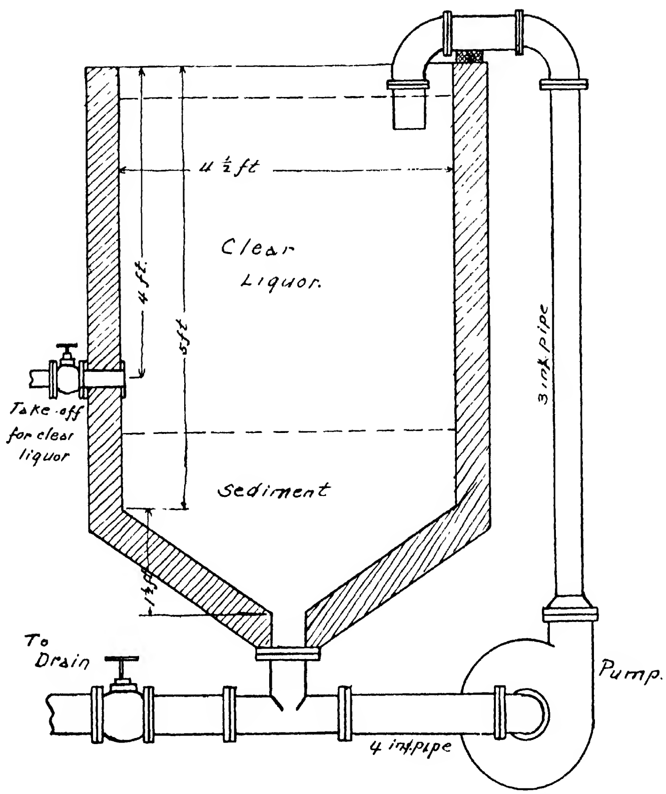


FIG. 153—Sketch of Apparatus for Preparing Solution of Bleaching Powder.

ine gas into milk of lime and thus obtained a solution of hypochlorite of lime. Later Labarraque in 1820 produced sodium hypochlorite solution which corresponded to but was cheaper than the Jevelle water. Improvements were constantly made in the methods of bleaching with chlorine, and in 1830 Tennant put on the market dry, solid chloride of lime or bleaching powder, and ever since this has been the principal chlorine bleaching agent.

A fresh solution of bleaching powder gives the same odor as the powder itself. The solution has an alkaline reaction, and when concentrated has a greenish yellow color, but dilute solutions are colorless. Occasionally the solution may exhibit a slight reddish color due to traces of manganese or iron compounds. When exposed to the air the solution rapidly absorbs carbonic acid, liberating hypochlorous acid and forming calcium carbonate which causes the solution to become cloudy.

$$2CaOCl_2 + CO_2 + H_2O = 2HOCl + CaCO_3 + CaCl_2$$

If the liquor is left quiet a thin scum of calcium carbonate will form on the surface, and this will protect the rest of the solution from further action by the air.

When treated with dilute mineral acids, bleaching powder, or its solution, liberates chlorine gas and forms the corresponding lime salt. The reactions are as follows: with hydrochloric acid

$$CaOCl_2 + 2HCl = CaCl_2 + Cl_2 + H_2O$$

with sulfuric acid

$$CaOCl_2 + H_2SO_4 = CaSO_4 + Cl_2 + H_2O$$

The author has found that the most economical method of preparing solutions of bleaching powder is to employ a system of agitation actuated by a pump. Such an apparatus is shown in Figure 153. The tank is first filled with water, the centrifugal pump is started and then the chloride of lime powder is thrown in. The circulation of the chloride of lime through the pump breaks the lumps into fine powder and serves to very intimately mix the bleaching powder with the water. The pump is run for about one-half hour, then the liquor is allowed to settle for 6 hours. This method of agitation gives a very rapid solution of the bleaching powder and exhausts the material more efficiently than the older methods of agitation where paddles were used. The tank is constructed of cement, and is of sufficient capacity for a drum (800 lbs.) of bleaching powder. The solution obtained in this manner will stand at about 10 to 12° Tw. (depending on the volume of the tank), which will be in the proportion of about 1½ gallons of water for each pound of bleaching powder. The volume allowed for sludge should be about 5 cubic feet for each 100 pounds of bleaching powder. Under the conditions given above there will be only about 0.7 percent of undissolved available chlorine in the sludge. The outlet pipe for the clear bleach liquor should be arranged at a sufficient height as to allow for the proper volume of the sludge. If this is not the case the time of settling will be much prolonged. In 6 hours time the amount of settling is about 95 percent of what it would be in 16 hours.

The following observations taken under actual mill conditions will illustrate this point:

Time occupied	Distance settled clear
1 hr. 36 min.	2 ft 0 in.
1 " 12 "	1 " 0 "
2 " 16 "	0 " 6 "
11 " 0 "	0 " 3 "

It is thus seen that in 5 hours 4 minutes the liquor settled clear 3 feet 6 inches, while in the next 11 hours it only settled a further 3 inches.

Another important factor in the efficient and rapid preparation of bleaching powder solutions is the temperature of the water employed. When the water is cold (50° to 60° F.) the rate of settling is very

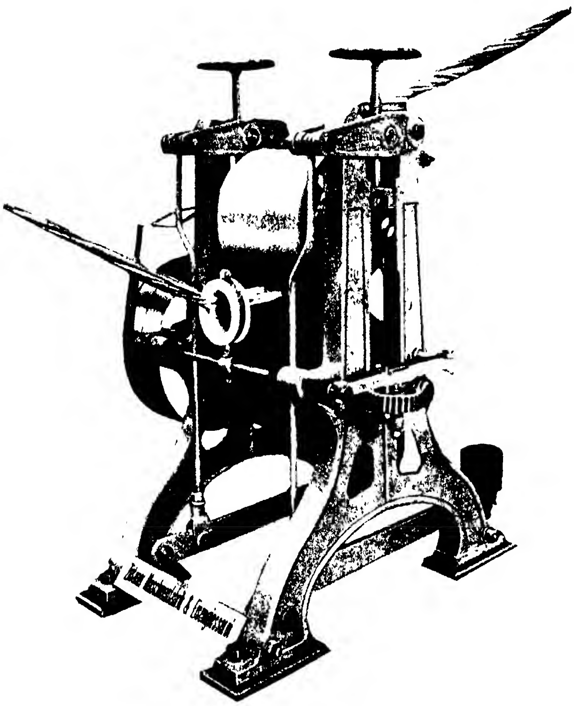


Fig. 155—Squeezer for Cloth in Rope Form.

slow; whereas when the temperature of the water is 75° to 85° F., the rate of settling of the sludge is greatly increased. This is shown by the following tests:

Temp. of water, F.°	50	85
Inches settled, per hr.	6	22
Degrees Tw. of solution	13	12
Cu. ft. of sludge per 100 lbs. of chemic	5.4	2.2

It is stated as a matter of practical observation that the water used for preparing a chloride of lime solution should be at a temperature of 75 to 85° F. The agitation or mixing should be continued for 20 minutes for all strength of liquors up to 16° Tw., as further time of agitation is simply wasted and makes the settling slower. The space al-

lowed in the tanks for the sludge should be 5 cubic feet for each 100 pounds of bleaching powder, and unless sufficient space is allowed for the settling of the sludge a great deal of time is wasted. In washing the sludge the agitation should only be carried out for 5 minutes.[14]

The sludge does not consist of bleaching powder, but of insoluble hydrate of lime suspended in the solution of bleaching liquor. Under the conditions of settling as given in the above method of preparing the solution, about 90 to 95 percent of the volume of the sludge will be liquor. From this it may be seen that after all the clear solution of chemic has been run off there is still quite a large amount present in the sludge. This, however, is present simply as the dissolved chemic, and not as insoluble matter in the sludge. To extract this residual amount, the tank should be filled up with fresh water and the pump circulated for about 5 minutes. The liquor is then allowed to settle again. In this manner about 98 percent of the available chlorine in the bleaching powder may be extracted and utilized.

The composition of the sludge obtained in the preparation of bleach liquors is of considerable interest and yet it has received but little study from the bleacher. According to the specifications contained in *Ger. Pat.* 195, 896 (for the preparation of solid calcium hypochlorite of high strength) calcium hypochlorite forms basic compounds with calcium hydroxide of the formulas $Ca(OCl_2)_2.2\,Ca(OH)_2$ and $Ca(OCl_2)_2.4\,Ca(OH)_2$. These compounds crystallize readily and are characterized by being difficultly soluble. Since these compounds no doubt exist in all commercial bleaching powder to some extent, it is natural to expect that they will be present in the sludge and will retain a certain amount of available chlorine. According to Lunge and Schäppli[15] ordinary bleaching powder sludge (dry) has the following composition:

	Percent
Calcium hydrate, $Ca(OH)_2$	59.28
Calcium carbonate, $CaCO_3$	27.81
Calcium hypochlorite, $Ca(OCl)_2$	5.98
Alumina and iron oxide	1.00
Water	5.42

There will generally result about 40 percent of sludge on the weight of the bleaching powder used.

[14] Griffin (*Jour. Soc Chem. Ind*, 1904, p 174) makes the following remarks concerning the preparation of bleaching powder solutions A bleaching powder of 38 to 39 percent of available chlorine will settle much better than one of lower chlorine strength. The quality of the water has an important influence on the results, as it affects the relative specific gravities of the solution and the insoluble matter A small amount of carbon dioxide in the water will cause a much more rapid settling Griffin finds that a bleach liquor of 6° to 7° Tw. is the most convenient to make, and this together with the first washing from the sludge will give a solution of about 4.2° Tw. Such a liquor is suitable for most purposes and requires a capacity of about 1 cu ft for 3 75 lbs. of good powder. Griffin recommends the following installation for preparing the solution: Two round or square concrete tanks with agitators and adjustable syphons leading to a storage tank having a capacity equal to the sum of the first two In one tank a mixture of 6° to 7° Tw. is made up and allowed to settle; the other tank contains the sludge from a former extraction, and this is filled up with fresh water, agitated and allowed to settle. The two liquors are then drawn off in equal volumes giving in the storage tank a liquor of about 4° Tw. The sludge from the second liquor is again agitated with water and settled and this weak liquor is used to wash the strong sludge from the fresh extraction. After the second washing the sludge is discharged and the tank is ready for a fresh charge of powder.

[15] *Chemische Industrie,* 1881.

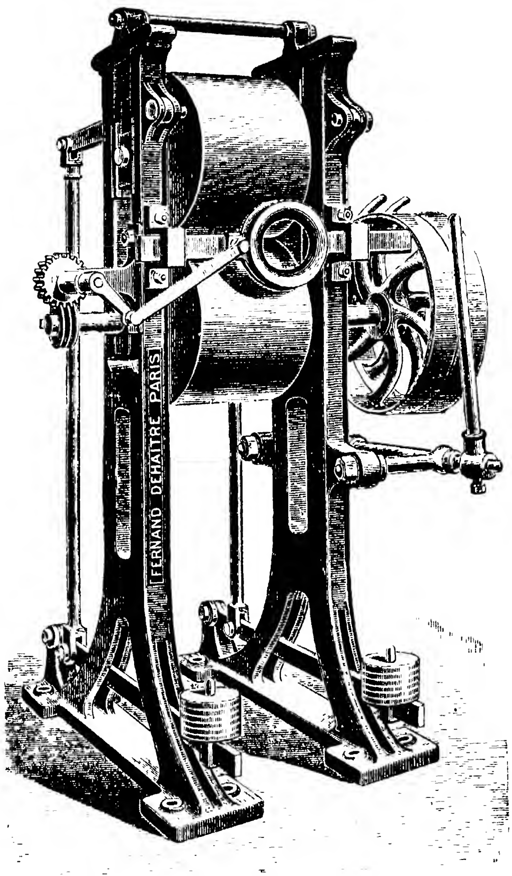


FIG. 156.—French Type of Bleach House Squeezer.

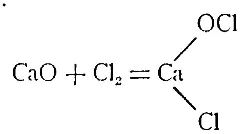
10. **Chemical Reactions of Chloride of Lime.**

The chemical behavior of chloride of lime with reference to its bleaching qualities is rather complicated, as it does not act directly on the coloring matter. It is generally supposed that the bleaching action of chloride of lime is due to the chlorine it is capable of liberating; but even so, the chlorine itself does not act directly as a bleaching agent. Dry chlorine gas does not produce any bleaching effect, and investigation has shown that the presence of moisture is necessary to cause the chlorine to destroy coloring matters. From this it has been supposed that the chlorine first acts on the water at hand, forming hydro-

chloric acid and liberating oxygen; and that the latter, at the moment of its liberation from its combination in water, is especially active chemically, and in this manner destroys the organic coloring matter which may be in contact with it. This action may be represented by the following equation:

$$Cl_2 + H_2O = 2HCl + O$$

Chloride of lime is obtained by allowing chlorine gas to act on slaked lime. The exact chemical nature of the compound has been a matter of considerable dispute, but it is now generally supposed that chloride of lime is an oxychloride of calcium, and its formation may be represented as follows:



This is perfectly in keeping with the formula $CaOCl_2$, which analysis shows to be the correct one for chloride of lime, and it also accounts for the chemical behavior of the compound. When chloride of lime is dissolved in water, it is decomposed into calcium chloride ($CaCl_2$) and calcium hypochlorite ($Ca(OCl)_2$) both of which are soluble:

$$2\ CaOCl_2 = CaCl_2 + Ca(OCl)_2.$$

The calcium chloride does not play any part in the bleaching process, but the calcium hypochlorite acts in the following manner: In the first place, as it is not a very stable compound it partially decomposes, in contact especially with organic matter, into calcium chloride and free oxygen, as follows:

$$Ca(OCl)_2 = CaCl_2 + 2\ O$$

In the second place, in the presence of acids, even such weak acids as the carbon dioxide in the air, calcium hypochlorite is decomposed into the corresponding salt of calcium and free hypochlorous acid:

$$Ca(OCl)_2 + CO_2 + H_2O = CaCO_3 + 2HClO$$

The hypochlorous acid so formed is readily decomposed into hydrochloric acid and oxygen:

$$HClO = HCl + O$$

It may also decompose, especially in the presence of heat or stronger acid, into water and free chlorine oxide:

$$2\ HClO = H_2O + Cl_2O$$

Carbon dioxide, or other acid, acting on dry chloride of lime liberates free chlorine, as follows:

$$CaOCl_2 + CO_2 = CaCO_3 + Cl_2$$

According to Jakocokin[16] chlorine in dilute solution is for the most part hydrolyzed, as follows:

$$Cl_2 + H_2O. = HCl + HO.Cl$$

[16] *Zeit. f. Physik. Chem.*, 1899.

The hypochlorous acid thus formed is the active bleaching agent. There is apparently very little direct chlorination of the fiber in ordinary bleaching operations.

Lunge has claimed that the action of solutions of chloride of lime may be enhanced by the addition of acetic or formic acid, whereby free hypochlorous acid and calcium acetate are at first formed:

$$Ca(OCl)_2 + 2CH_3COOH = 2HClO + Ca(C_2H_3O_2)_2$$

The hypochlorous acid giving up oxygen is converted into hydrochloric acid, which acting on the calcium acetate furnishes calcium chloride and free acetic acid again, and this latter reacting with a fresh quantity of chloride of lime carries the same series of reactions through once more. It is claimed that in these reactions the hydrochloric acid is never liberated really in the free state, for as soon as it is formed, it reacts with the calcium present to give acetic acid, hence there is never present any hydrochloric acid capable of attacking the cotton; also as there are no insoluble calcium salts present the after treatment with an acid bath may be dispensed with.

According to Ditz[17] in the preparation of bleaching powder a compound is first formed consisting of calcium oxide in combination with the chlorinated product:

$$2\,Ca(OH)_2 + Cl_2 = CaO.Ca\begin{array}{l}\diagup OCl\\ \diagdown Cl\end{array}.H_2O + H_2O$$

as the reaction proceeds the temperature rises, and this intermediate compound reacts with water to give:

$$CaO.Ca\begin{array}{l}\diagup OCl\\ \diagdown Cl\end{array}.H_2O + H_2O = Ca(OH)_2 + Ca\begin{array}{l}\diagup OCl\\ \diagdown Cl\end{array}.H_2O$$

From the calcium hydrate thus liberated a fresh quantity of the intermediate product is formed, and at the increased temperature the reaction proceeds as follows:

$$4\,Ca(OH)_2 + 3\,Cl_2 = 2\,Ca\begin{array}{l}\diagup OCl\\ \diagdown Cl\end{array}.H_2O + CaO.Ca\begin{array}{l}\diagup OCl\\ \diagdown Cl\end{array}.H_2O + H_2O$$

These reactions proceed with absorption of chlorine until as a final product there is obtained:

$$Ca\begin{array}{l}\diagup OCl\\ \diagdown Cl\end{array}.H_2O$$

[17] *Färber-Zeitung,* 1905.

It is not possible, however, to obtain all of the product in this form, as there always occurs a considerable amount of the intermediate product:

$$\mathrm{CaO.Ca}\begin{array}{l}\diagup\mathrm{OCl}\\ \diagdown\mathrm{Cl}\end{array}\mathrm{.H_2O}$$

If the bleaching powder consisted altogether of the former compound, it would give no precipitate of lime when dissolved in water:

$$2\,\mathrm{Ca}\begin{array}{l}\diagup\mathrm{OCl}\\ \diagdown\mathrm{Cl}\end{array}\mathrm{.H_2O} \rightarrow \mathrm{Ca(OCl)_2} + \mathrm{CaCl_2} + 2\,\mathrm{H_2O}$$

The formation of the lime precipitate results from the action of water on the second compound as shown in one of the above reactions. As commercial bleaching powder always gives rather copious precipitate (sludge) of lime when mixed with water it would indicate, according to Ditz, that the intermediate compound was present in considerable proportion.

Beyrich, in 1877,[18] suggested the addition of oxalic acid to the bleaching bath of chloride of lime, and states that in this way a much stronger bleaching effect can be obtained, that the fiber is not injured and that a previous boiling-out operation is not required; also by warming the chemic bath to 100° F. the period required for bleaching is materially reduced without injury to the goods. In this method, it may be said, that the oxalic acid on the one hand precipitates the lime (as oxalate of lime) and on the other hand sets free hypochlorous acid so that the bath would necessarily show a much more rapid bleaching action, but contrary to the claims of the inventor it is not possible to obtain a satisfactory white without a previous boiling-out of the goods in a kier. It does not seem that this process has been adopted at all in actual practice.

With reference to the question of the formation of solid bleaching powder and bleaching solutions it is remarkable that in all reactions characteristic of the former, water plays apparently a very essential rôle. The best bleaching powder according to Lunge and Schappli[19] is obtained from lime containing 27.5 percent of water instead of the 23.5 percent which would correspond to the formula of $Ca(OH)_2$. If the lime contains either more or less water, less chlorine will be absorbed. Commercial bleaching powder in fact contains 16 to 17 percent of water.

A large amount of bleaching powder is now prepared by electrolytic methods; that is to say, the chlorine used is obtained in the elec-

[18] *Ger. Pat.* 2148.
[19] *Dingler's Polytechnische Journal*, vol. 237, p. 63.

trolysis of sodium chloride, and this chlorine is passed over the slaked lime to form the bleaching powder. The other product of the electrolytic reaction is metallic sodium, and this is employed for the preparation of either caustic soda or sodium peroxide, both of which compounds are also extensively employed in the bleaching of textile fibers. So it may be said that the electric current plays an important part at the present time in the art of bleaching. The bleaching powder obtained by the use of electrolytic chlorine has been difficult to prepare commercially, on account of the fact that the chlorine so obtained is rather dilute, being mixed with air and carbon dioxide, and it is only within recent years that successful methods for the commercial preparation of such bleaching powder have been devised. It is said that the

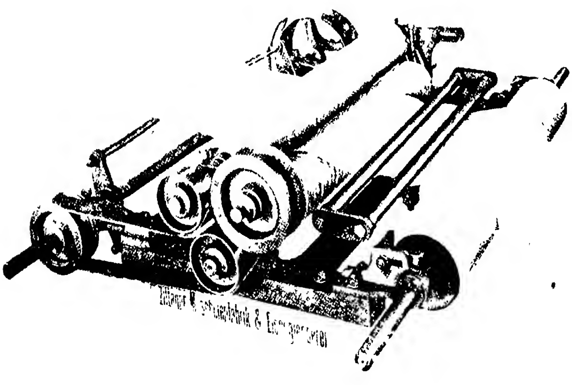


FIG. 157.—Opener for Cloth in Rope Form.

chief difficulty experienced is due to the presence of carbon dioxide gas. The mixed gases containing the chlorine should also be dry, and the slaked lime should not contain more than 5 percent of water above that required for water of hydration, or about 28 percent on the weight of the lime.

The question as to whether bleaching powder is a mixture of calcium hypochlorite and calcium chloride or a single molecular compound corresponding to an oxychloride is really more a question of molecular aggregation than a distinctly chemical difference. Fresenius held that bleaching powder was an ordinary mixture of the two salts, for on treating bleaching powder with successive small quantities of water he found a much larger ratio of calcium chloride to calcium hypochlorite in the first extract than in the last; this fact being explained by the greater solubility of the calcium chloride.

11. Action of Carbon Dioxide on Bleaching Powder.

The action of carbonic acid on bleaching powder is a progressive one and requires but a small amount of carbonic acid for the gradual decomposition of a large amount of bleaching powder, as may be seen by the following equations:

(a) $CO_2.H_2O + 2\,CaOCl_2 = 2\,HOCl + CaCO_3 + CaCl_2$
(b) $2\,HOCl = 2\,HCl + O$
(c) $2\,HCl + CaCO_3 = CaCl_2 + CO_2.H_2O$
(d) $HCl + CaOCl_2 = CaCl_2 + HOCl$

The carbonic acid plays the part, as it were, of a catalyzer in starting the reaction of decomposition, which then is maintained by the liberation of the hydrochloric acid through the spontaneous decomposition of the hypochlorus acid at first formed.[20]

In the practical bleaching of cotton it has been noticed that between the morning and evening of a day's work a gradual diminution takes place in the amount of bleaching powder required for every pound of the same sort of material bleached. This is said to be due to a gradual acidification of the bath by carbonic acid.

The fact that carbonic acid liberates all the chlorine from bleaching powder led Lunge to ascribe to it a formula somewhat different from that given to ordinary hypochlorite, although it is also admitted that when bleaching powder is dissolved in water the solution contains both calcium hypochlorite and calcium chloride. The dry powder of chloride of lime, however, cannot be considered as such a mixture. In this case, since carbonic acid cannot decompose calcium chloride, the entire amount of the chlorine would not be available. Therefore, according to Lunge, the atom of chlorine directly united with the calcium in bleaching powder has different properties from those of the same element in calcium chloride.

The liberation of the entire amount of chlorine in bleaching powder by carbonic acid may be better explained, however, by considering the reaction between chlorine and lime as being of the reversible type; in which case it would be represented by the following formula: $2\,Ca(OH)_2 + 2\,Cl_2 \longleftrightarrow CaCl_2 + Ca(OCl)_2 + 2\,H_2O$ (or slaked lime + chlorine$\longleftrightarrow$calcium chloride + calcium hypochlorite + water), thus representing bleaching powder in the same manner as it would be when in solution in water. This is more or less borne out by the fact that the peculiar odor of "bleach" resembles that of free hypochlorous acid rather than that due to the presence of free chlorine.[21]

[20] Taylor and Higgins both describe the rôle played by carbonic acid in bleaching in another manner. The first assumes that the carbon dioxide reacting with chloride of lime and similar bodies, sets free only chlorine and no hypochlorous acid. In the ordinary process of bleaching, therefore, the free chlorine becomes the chief bleaching agent and not the hypochlorous acid. Higgins explains the action of carbon dixodide on chloride of lime according to the following two equations:

$$Ca(OCl)_2 + CO_2 + H_2O = CaCO_3 + 2\,HOCl, \text{ and}$$
$$2\,HOCl + CaCl_2 + CO_2 = CaCO_3 + 2\,Cl_2 + H_2O.$$

The reaction expressed in the second equation is reversible. In bleaching the chief effect is assumed by the hypochlorous acid, though some part is also taken by the nascent chlorine (see *Chem. Zeit.*, 1911, p. 464). In a later communication, however, Higgins states (*Chem. Zeit.*, 1912, p. 189) that the bleaching effect is due to nascent oxygen.

[21] In an investigation on the action of carbon dioxide in the bleaching process, Higgins (*Chem. Soc. Proc.*, 1911, p. 67) states that on adding calcium chloride to lime water the rate of solution of carbon dioxide from the air in the liquor is increased, and this fact probably

The reversibility of this reaction will also explain why it is impossible to prepare bleaching powder containing the theoretical amount of chlorine. On treating bleaching powder with carbonic acid gas, the chemical equilibrium is disturbed; calcium carbonate being formed and

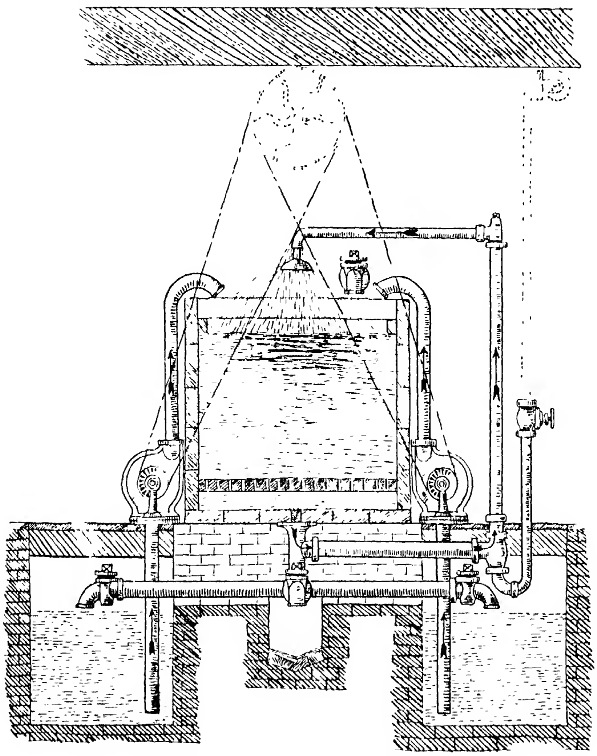


FIG. 158.—Chemic and Scouring Box.

hypochlorous acid set free. This latter reacts with the calcium chloride liberating chlorine, and since the latter cannot act upon the calcium carbonate, the reaction goes on until the whole of the calcium in the bleach is converted into carbonate, and the whole of the chlorine is liberated.

accounts for the observation that the addition of calcium chloride to a bleaching powder solution increases its bleaching efficiency. On exposing bleaching powder solution to the air, the free lime contained in the solution is deposited as calcium carbonate, and then the carbon dioxide of the air acts on the other calcium salts present in the solution. It is the latter action that causes the exposed bleaching powder solution to have a high bleaching efficiency. Common salt added to sodium hypochlorite solution also increases the bleaching efficiency to some extent, and this is also true of other neutral salts of sodium. Also equivalent proportions of common salt and calcium chloride have approximately the same effect in increasing the activity of bleaching powder solutions. These effects are probably due to the increased attraction of the carbon dioxide of the air by the neutral salt solution.

In connection with this action of carbonic acid on bleaching powder, it may be said that a solution of bleaching powder is only attacked by carbonic acid at a temperature of 160° F. or over. Bleaching powder itself is decomposed at 160° F. more quickly by moist carbonic acid than the dry gas, and if the bleaching powder be first dried by having its moisture absorbed over sulfuric acid, it is hardly attacked at all by the carbonic acid.

The chlorine evolved when bleaching powder is decomposed by carbonic acid always contains hypochlorous acid. When a current of moist air is passed over heated bleaching powder it produces calcium chlorate and oxygen, but no chlorine is evolved. But if a current of dry air is used at a temperature of 90° to 105° F. the same products are formed together with chlorine, and at 200° F. most of the available chlorine is removed.

Contrary to chloride of lime liquors, electrolytic bleach liquors by the action of the carbon dioxide of the air can never form free chlorine, since the bicarbonate which is produced in the reaction will effectually prevent this condition; on this account bleaching with electrolytic liquors should be somewhat less dangerous to the fiber.

12. Use of Acids in Bleach Liquors.

Baeyer (in 1891) recommended the addition of boric acid to bleach liquors for the purpose of liberating hypochlorous acid, but such a process does not seem to have ever been used in practice. Dépierre suggested a modification of Lunge's method by impregnating the fabric with the chemic, then spraying with dilute acetic acid and steaming. According to Lauber, such a process has been very successfully employed in calico printing. Formic acid may be used in the same way. Another process based on the same idea is to first rinse the goods in a dilute acid bath before running them into the chemic. This method is indeed the simplest way to proceed if a quick bleaching operation is desired. Hadfield-Sumner[22] describe an apparatus whereby the goods are impregnated with chemic and then subjected to the action of acetic acid vapors.

The use of acid in connection with bleach liquors is also to be found in the Thies-Herzig special process of bleaching. If the addition of acid, however, is not very carefully regulated the velocity of bleaching will become too great and the bleach will be uneven or oxycellulose may be developed.

The addition of acid to hypochlorite bleach liquors for the purpose of neutralizing the alkalinity is accompanied by certain dangers which may be avoided by using magnesium chloride in place of acid. In this case there is formed calcium (or sodium) chloride and difficultly soluble magnesium hydrate. An excess of magnesium chloride is without particular harm. The precipitated magnesium hydrate is allowed to settle and there is then obtained a bleaching liquor having rapid bleaching properties. Such a chemic has been used to quite an excess in England. Hodges also prepares magnesium hypochlorite with

[22] *Ger. Pat.* 107,093.

magnesium sulfate and a solution of chloride or lime. Calcium sulfate is precipitated and is allowed to settle, after which the clear liquor may be used directly for bleaching, or it may be "activated" by the addition of a little soda ash. The latter in this case reacts with the excess of magnesium sulfate present to form sodium sulfate, basic magnesium carbonate and free carbonic acid, the last increasing the activity of the solution. Such bleach liquors containing magnesium compounds have a greater activity if they are slightly alkaline in reaction; however, a greater bleaching velocity is not a special characteristic of magnesium hypochlorite. The different salts of hypochlorous acid, however, show certain differences in dissociation, and the lower bleaching activity of chloride of lime is more or less dependent on the alkalinity of the solution as a result of the content of calcium hydrate present. Bregeard [23] recommends the addition of zinc sulfate to the chloride of lime solution for the purpose of increasing the bleaching activity by decreasing the alkalinity.

[23] *Ger Pat.* 20,177.

Chapter XVII.

The Bleaching of Cotton (*Cont.*).

1. Alkalinity of Bleaching Powder Solutions.

When bleaching powder is dissolved in water there is always more or less free lime to be found in solution. The quantity of free lime taken up appears to vary inversely with the concentration, calculated upon the chlorine strength. The proportion of free to total combined lime (CaO) in bleaching powder itself has been found by O'Shea [1] to be about 1 :2.4; one-half of the combined lime, however, on solution reverts to calcium chloride ($CaCl_2$), the other half remaining combined with the chlor-oxygen group. In a mixture of bleaching powder and water there is nearly as much free lime as there is lime combined as hypochlorite. In the clear solution of bleaching powder, however, there is only a very small proportion of hydrate of lime present (1 to 2 percent), as at the best it could only be a saturated solution of lime water (1 :760), and in the presence of the large amounts of other dissolved lime salts it would represent a much less concentration. Consequently the clear solution of bleaching powder forms a very nearly neutral liquor.[2]

The content of dissolved hydrate of lime in solutions of bleaching powder appears to be practically independent of the concentration, as is shown by the following figures which represent the analyses of filtered bleach liquors prepared from 1000 c.c. of water with varying amounts of bleaching powder:

Bleaching powder gms. per liter	Content CaO gms. per liter	Avail. chlorine gms. per liter	Avail. chlorine after 20 days gms. per liter	Loss Percent
25	0.873	5 86	4.97	15.15
50	0 884	11.36	10.51	7.50
100	0.918	21.80	20.73	4.89

[1] *Jour. Chem. Soc.*, 1883, 417.

[2] The alkalinity of the chloride of lime bleach liquor, that is to say, its content of calcium hydrate $Ca(OH)_2$, varies with the proportion of water originally used in preparing the solution. If this proportion is changed the quantity of acid necessary to be added for neutralization will also change. A bleach liquor, for instance, which has been prepared by extracting fresh quantities of chloride of lime with water employed for exhausting a previous lot will have a much higher alkalinity (and will consequently require the addition of much more acid for neutralization) than a liquor prepared from a concentrated chemic of an equivalent content of active chlorine. Furthermore, in this connection, it must be particularly noticed that the addition of acid increases the bleaching velocity only up to a certain point; when all the hypochlorite salt is decomposed, then further addition of acid will only liberate chlorine ($HOCl + HCl = H_2O + Cl_2$).

It will also be noticed from the above table that the loss in strength of the chemic solutions is less for the strong solutions than for the weak, probably due both to the slightly increased alkalinity and the lessened degree of dissociation.

2. Other Forms of Chloride of Lime.

Calcium hypochlorite of high concentration has been prepared by saturating milk of lime with chlorine gas. The liquor is then filtered and concentrated by evaporation in a vacuum in order to avoid the decomposition of the calcium hypochlorite. By this method solid crys-

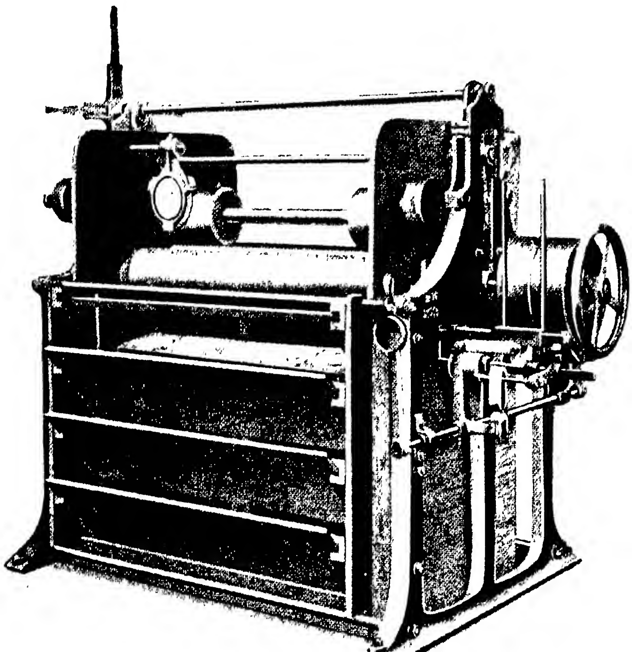


FIG. 159.—Bleacher's Liming, Souring and Washing Machine.

talline calcium hypochlorite may be obtained containing from 80 to 90 percent of active chlorine.

Instead of employing chloride of lime as the bleaching agent, other chlorine compounds may be used. Even solutions of free chlorine have been tried, but this method does not appear to be a success, both on account of its expense, and by reason of the fact that solutions of free chlorine gas are not as effective in their bleaching action as bleaching powder or chlorine in a condition of just being liberated from its chemical compounds; the so-called "nascent" state. Attempts

have been made to convert free chlorine gas into this condition by "ionizing" it by means of an electric spark, and some degree of success is claimed to have been attained. Instead of using solutions of bleaching powder prepared from the dry powder, a solution prepared by saturating milk of lime with chlorine gas has been put on the market, and has proved very effective. Such a solution contains a large proportion of calcium hypochlorite, and if preserved in a cool place will retain its strength for a long period of time.

3. Stability of Bleaching Powder Solutions.

In order to study the stability of hypochlorite solutions Higgins has utilized the reaction of bleaching powder solutions with copper oxide. In this reaction oxygen is given off and the rate at which the oxygen is evolved is employed to measure the stability of the solution. In carrying out this test a 100 c.c. Jena flask is used fitted with an india-rubber stopper through which a glass tube is passed. This tube is bent twice at right angles outside the flask and terminates under a burette filled with, and standing in a basin of, water. The bleaching powder solution (100 c.c.) and the powdered copper oxide (1 gram) are placed in the flask and the amount of oxygen evolved is measured at intervals.

It is well-known that the more stable a solution of hypochlorite is the less readily it bleaches, and any circumstances which make the solution less stable increase its bleaching effect. Thus the addition of alkali increases the stability and decreases the bleaching effect, whereas the addition of neutral salts is attended by opposite results in each case. The application of heat decomposes the hypochlorite, and also stimulates the bleaching action of the solution. The effect of sunlight on hypochlorite solutions was investigated by White, who found that bleaching powder solution under the action of sunlight gave off pure oxygen, or rather that the evolution of oxygen from hypochlorite solutions was greatly accelerated by exposure to the sun's rays. Moreover, all bleachers know the value of the sun's rays in the bleach-house, because they stimulate the bleaching action of hypochlorites; this increased efficiency again forms a parallel with decreased stability, and points to the conclusion that the pure oxygen which is evolved in the one case performs the bleaching in the other. The evolution of the oxygen is quickened by removing the gas from the solution, and in the bleaching cistern this removal is performed by the action of the oxidizable matter present..

The stability of solutions of bleaching powder seems to be somewhat dependent on whether or not they are prepared in a concentrated or dilute form. This is shown by the fact that if a strong bleach liquor is first prepared and then diluted to a definite strength it is far less stable than if the dilute liquor were prepared directly, as is demonstrated by the following test: a concentrated liquor of bleaching powder was prepared, settled, filtered, and then diluted to a strength of 4.10 grams of available chlorine per liter; then a dilute liquor of approximately the same strength was prepared directly from bleaching powder;

the first solution in 8 days open lost 13.17 percent strength, and closed, 11.22 percent, while the second solution lost only 7.62 percent and 4.05 percent respectively. The explanation of this is probably due to the fact that the second solution will contain a somewhat higher proportion of free caustic lime ($Ca(OH)_2$). Higgins concludes that the bleaching effect of hypochlorite solutions is proportional to the rate at which these solutions evolve oxygen gas when in contact with copper oxide.

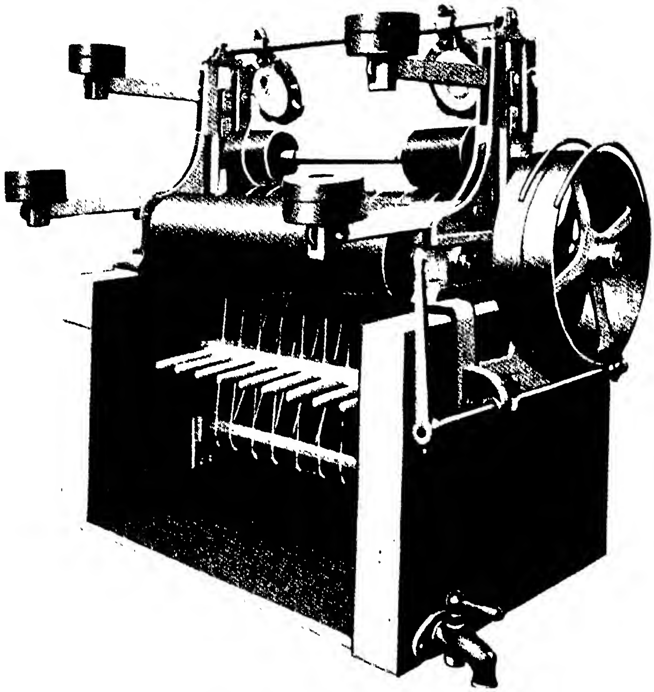


Fig. 160.—Machine for Chemicking and Souring.

4. Bleaching with Chloride of Lime.

The bleaching process proper, or the treatment with chloride of lime, is generally called *chemicking*, and the bleach liquor is known as the *chemic*. The bleaching is effected by steeping the goods in a clear solution of chloride of lime standing at ½° to 2° Tw. The chemicking is usually carried out in either wooden or cement tanks; the latter are preferable, as wood is rapidly attacked by the solution of chloride of lime. The proper solution of the chloride of lime is a point of considerable importance, not only from considerations of economy, but also from the fact that improperly prepared solutions may act very injuriously on the goods. The use of strong solutions of bleaching

powder must be avoided, as these act in a very injurious manner on the cotton, both through their action as strong oxidizing agents (thus forming oxycellulose), and by reason of the fact that large amounts of free hydrochloric acid are generated in the bath. By the use of alkaline solutions the formation of this acid is prevented, but at the same time the energy of the bleaching action is also considerably moderated. If the bleaching bath is too weak there is liability of lack of penetration, and the outside of the fiber will be bleached, but the in-

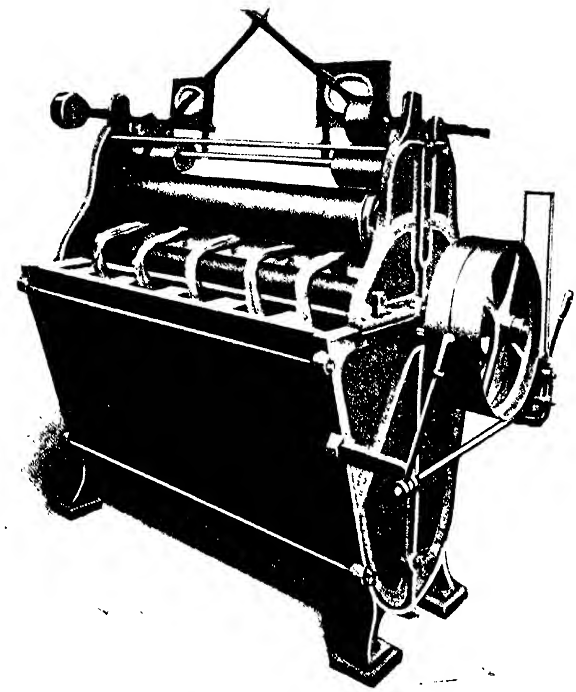


FIG. 161.—Chemic Box.

side will not, and as a result, the goods are liable to become yellowish again on exposure and after the lapse of time. The best strength of chloride of lime solution to use for bleaching under ordinary conditions is about 1° to 2° Tw. Solutions of greater strength than this are dangerous to use on account of the liability to tender the cotton.

The concentration of the chemic solution, or rather the total quantity of the active chlorine in the bath, should be regulated according to the amount of impurities in the goods. It is not only the concentration of active chlorine that counts, but also the quantity of chemic in contact with the material. Over-oxidation or "burning" of the goods is possible

even in relatively weak chemics provided the bath is of sufficient volume, for if the bleaching action is continued for a sufficient length of time the effect of the chlorine will be an accumulative one. The amount of total chlorine in the bath should not exceed a certain ratio to the quantity of the goods. The chlorine consumption in bleaching quickly reaches a definite value which corresponds to the oxidation of the easily destroyed substances which it is the object of the bleaching to remove.

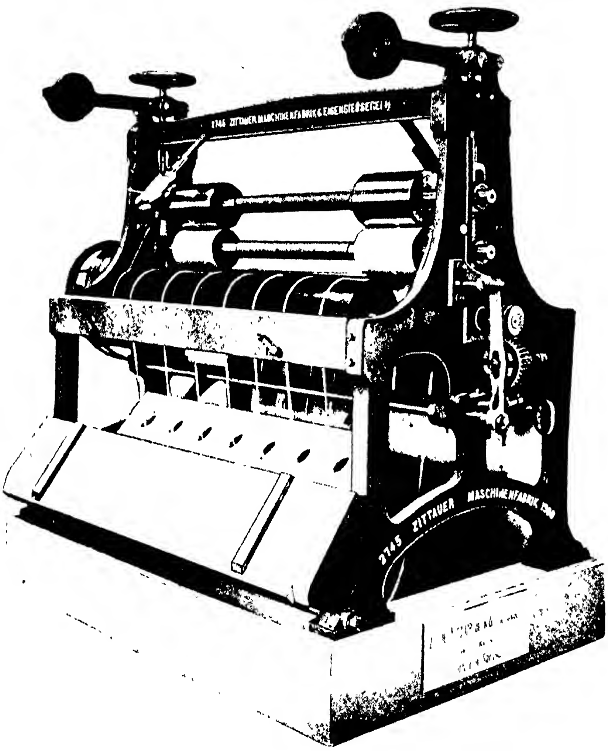


FIG. 162.—Saturating Machine for Chemic or Sour.

The more difficultly oxidizable substances, such as the cellulose itself, are only acted upon slowly. The stronger the original concentration of the chemic the more rapid will be the oxidation of the impurities, and the shorter, in consequence, must be the bleaching action in order to avoid the attack on the cellulose. The chlorine consumption is very seldom such as to lead to the complete exhaustion of the bath. There always remains, even after the most extended period of bleaching, a certain amount of active chlorine still in the bath, and also in the goods themselves, so that the latter have to be thoroughly washed in order to

set free the easily broken up hypochlorous acid, or be treated with antichlor. Solutions that are acidified or heated exhaust much better than those that are alkaline and cold.

Ebert and Nussbaum by a series of experiments have shown that if the diffusion velocity of the hypochlorite is proportional to the concentration, the velocity of bleaching is almost independent of the concentration, and is determined by the temperature, but principally by the acidity. If there is a deficiency of hypochlorite, then the bleaching velocity is determined by the resulting slower diffusion, etc.

It is almost impossible to decide in a general way just what are the proper limits for the chlorine concentration of chemics in order to avoid injury to the fiber and yet give the most efficient bleaching results. It is sometimes better policy to give a rapid short bleaching in an energetic chemic rather than use one whose bleaching properties are slow, and, in consequence, necessitating a longer exposure of the goods to the bath. In using energetic liquors, however, and a short treatment, there is danger of lack of uniformity owing to improper or incomplete circulation and diffusion. The conditions of the chemic solution should be studied with reference to the character of the goods to be bleached as well as the other factors involved, as what might be satisfactory for one set of conditions might be totally unfit for others. In the action of the chemic, proper and close consideration should be given to the adequate diffusion of the active bleaching compounds through not only the goods in mass but also through the ultimate fiber itself. In the use of warm or acid chemics where the bleaching energy is very active and rapid, there is always a possibility of lack of proper diffusion of the chemic through the fiber, with the result that while the outer portion of the fiber is very energetically bleached (even to the point of formation of undue proportions of oxycellulose) the inner portion may be insufficiently bleached, a condition which is very liable to give rise to certain objectionable defects in the bleached goods later.

Solutions of chloride of lime of a less chlorine strength than 1.25 grams of chlorine per liter (½° Tw.) do not appear to exert any injurious action on the strength of the cotton fiber, even at a temperature as high as 80° F. When a strength of about 3 grams of chlorine per liter (1° Tw.) is reached, the cellulose of the fiber is gradually attacked with the formation of oxycellulose and hydrocellulose, and a consequent disorganization of the structure of the fiber. The action of the chloride of lime solutions on the cotton fiber is not perhaps so much due to the hypochlorite as to the free lime which is present in nearly all commercial grades of bleaching powder. This acting in the presence of an oxidizing agent (the hypochlorite or chlorine) rapidly attacks the cellulose of the fiber. This probably accounts for the fact that magnesium hypochlorite prepared by the electrolytic method has but little injurious action on cellulose, as there is no caustic alkali present.

A simple method of applying the bleach liquor is to use an ordinary washing machine for containing the solution, the goods are run through this and piled up and exposed to the air for several hours, or even overnight; after which they are soured. The goods before treatment with

the bleaching solution should not be too saturated with water, as the chloride of lime will be too much diluted as it is absorbed by the fiber.

Tailfer[3] records some interesting facts concerning the amount of chlorine required in the practical bleaching of cotton goods. In one example 850 kilos. of cotton ribbons were used, and these required 5,500 liters of bleach liquor, from which was absorbed during the bleaching an equivalent of 385 liters of gaseous chlorine; the total

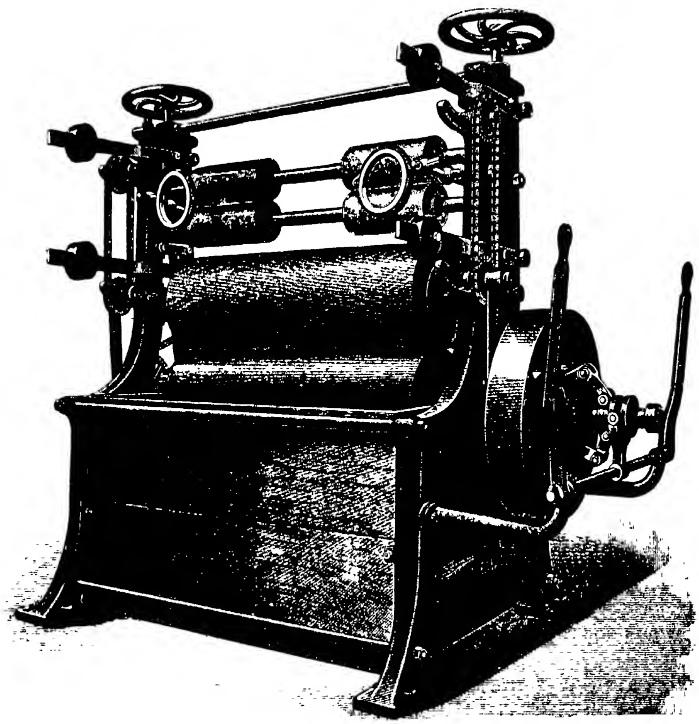


FIG. 163.—French Type Chemicking and Souring Machine.

quantity of chlorine contained in the liquor was 2.2 liters per kilo. of fabric, and the amount absorbed was 0.45 liter per kilo. of fabric. In a second example, 1,350 kilos of cambric were bleached with 31,200 liters of liquid, the total content of chlorine in which was 7,488 liters. The amount of gaseous chlorine absorbed in this case was 1.6 liters per kilo. of fabric. In a third example, 2,000 kilos. of cambric were chemicked for the second time in 39,000 liters of liquid of 0.21° chlorometric strength; after 2 hours' steeping the strength had fallen to 0.20°, after 4 hours to 0.19°, showing that the chemic had no action after the

[3] *Bleaching of Linen and Cotton*, p. 113.

first 4 hours, and the fabrics should have been withdrawn at the end of that time. The total quantity of chlorine originally present was 39,000 x $0.02 = 780$ liters; hence, each kilo. of fabric absorbed 0.39 liter of chlorine. The total quantity of liquor regained, however, only amounted to 30,000 liters, the rest being retained, it represented 39,000 x $0.19 = 2,490$ liters, or 1.24 liters per kilo. of goods. This is equivalent to approximately 0.4 pound of chlorine per 100 pounds of goods, and if reckoning that each pound of chlorine thus utilized requires about 3 to 4 pounds of bleaching powder to start with, we have the amount of the latter as 1.2 to 1.6 pounds per 100 pounds of goods.

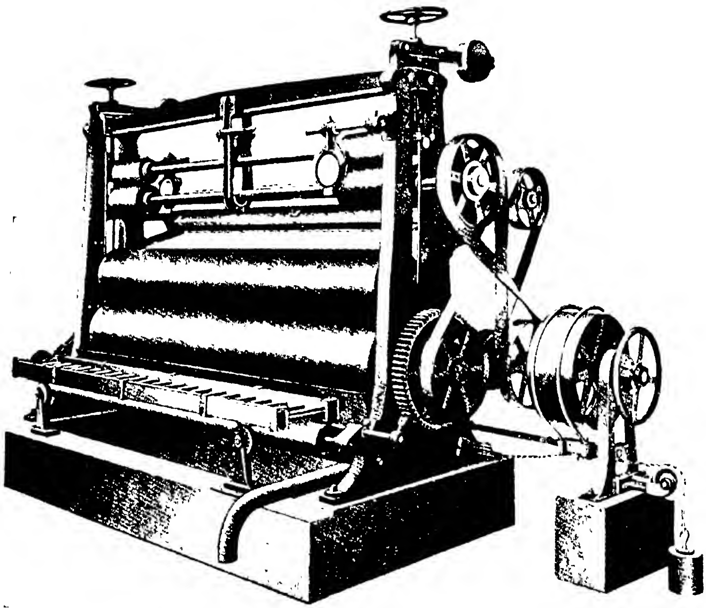


FIG. 164.—Slack Washing Machine.

The French chlorometric degree represents the number of liters of gaseous chlorine contained in one liter of the solution.

The strength of chemic required in bleaching cotton will depend to a great degree on the nature of the goods as well as other circumstances such as the thoroughness of boiling-out, the temperature of bleaching, the method of treating the goods and the degree of whiteness desired. For ordinary purposes, however, where a very good boil-out has been given the bleach liquor should show a strength of about 3 grams of available chlorine per liter, which corresponds to a freshly prepared chloride of lime solution of about 1° Tw. With chemics prepared from chlorine and alkali the content of available chlorine will be considerably less for the same hydrometer reading in degrees Tw., but

these will nevertheless have about the same bleaching efficiency as the chloride of lime. In the case of goods containing low grade carded yarns where shives and motes (sometimes very aptly called by the bleacher "sticks") occur in large quantities, it may be necessary to employ stronger chemics in order to clear up the goods. Care must be had, however, not to use too strong a chemic, as this results in the formation of oxycellulose and the tendering and rotting of the material. The use of a chemic of over 3° Tw. (8 grams of available chlorine per liter) is always dangerous, and even this strength should never be used except under carefully regulated conditions. Rather than use very strong solutions it is better to repeat the bleaching operations several times with weak liquors. It may also be remarked that solutions of sodium hypochloride may be used in higher strengths than chloride of lime with less danger to the goods. The strength of the chemic, however, is to be studied in relation to the nature of the solution and its resulting bleaching activity and the temperature at which it is used.

5. Temperature of Bleaching.

Temperature has considerable effect on the rapidity of decomposition of the hypochlorite solution. According to Foerster and Jorre a rise in temperature of 7½° C. (= about 13° F.) doubles the velocity of decomposition, and Abel has shown that the acceleration is greater in the case of alkaline solutions than with neutral or acid solutions. Therefore, it is natural to expect that bleaching would take place quicker in warm than in cold solutions. This fact is recognized in practice, and it is found that bleaching takes place faster in summer than in winter. While it is possible to shorten the bleaching reaction by using warm hypochlorite liquors, it must be remarked, however, that such chemics must be used with great care on account of the great danger of the formation of oxycellulose and the consequent weakening of the fiber. In the bleaching of coarse cotton goods made from low-grade carded yarns contaminated with a large amount of motes and shives, it may at times be found expedient to use a chemic which is warmed to 95 or 100° F. The use of higher temperatures should be avoided as an improper and dangerous practice. In the bleaching of paper pulp it is quite common practice to accelerate the action of the chemic by heating to about 100° F. Sometimes in the bleaching of other coarse vegetable materials (such as reeds, plait, etc.) the same practice is used. It is also quite usual in the bleaching of jute and sometimes even in bleaching linen, though in the latter case warm chemics should not be used except for low-grade and coarse yarns or fabrics. In ordinary bleaching processes, however, there is no objection to warming cold hypochlorite liquors to a practical bleaching temperature of 80° F., provided, however, that proper care is taken to avoid local overheating.

While the moderate heating of chemic solutions shows an acceleration of the bleaching reaction, if the temperature is raised too high the bleaching activity shows a rapid decline. This is caused by the rapid

formation of chlorate at the higher temperature, and *the chlorate possesses no bleaching power.*

The use of warm chemics is only of advantage to the bleacher when a rapid bleaching effect is desired, as in the comparatively rapid passage of yarn through the chemic, or in rapid continuous bleaching systems for cloth where the fabric is impregnated with the chemic and then is run over warm drying cylinders or through a steam chest. Such rapid methods of bleaching, however, nearly always show an imper-

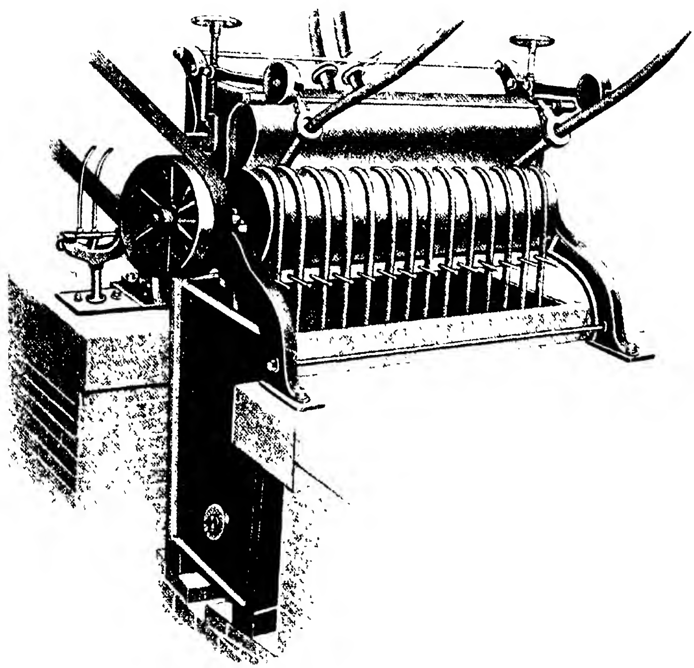


Fig. 165.—Showing Operation of Liming and Souring Machine.

fectly penetrated bleach, and this must be balanced up against the saving in time and cost of treatment.[4]

Descriptions of methods of bleaching sometimes to be met with in which cotton is boiled with mixtures of hypochlorite and alkali, are to be taken *cum grano salis* as far as their practicability is concerned, as they lack the elements of common sense and sound technique.

When a warm chemic is used it is important to properly regulate the quantity of the bleach bath as well as the concentration of active chlorine therein, for in this case weak though large baths may cause

[4] Investigation has yet to determine if a warm bleach is of any particular advantage in the saving of chemicals, appearance of the fiber and permanency of the white, as there is lack of any definite data on this subject derived from practical work.

an over-oxidation of the goods because the decomposition of the hypochlorite is both more rapid and more complete and the entire amount of the oxygen set free enters quantitatively into the reaction. In using warm chemics, therefore, the total chlorine content of the bath should be regulated in accordance with the quantity of goods to be bleached, in order to avoid the danger of the formation of oxycellulose.

Blackmann[5] recommends in his process a bleaching temperature of 130° to 160° F., but this is certainly too high and would be dangerous to use in practice. Perhaps in the use of electrolytic sodium hypochlorite liquors containing a high proportion of common salt such high temperatures may be used with more safety to the goods than would be

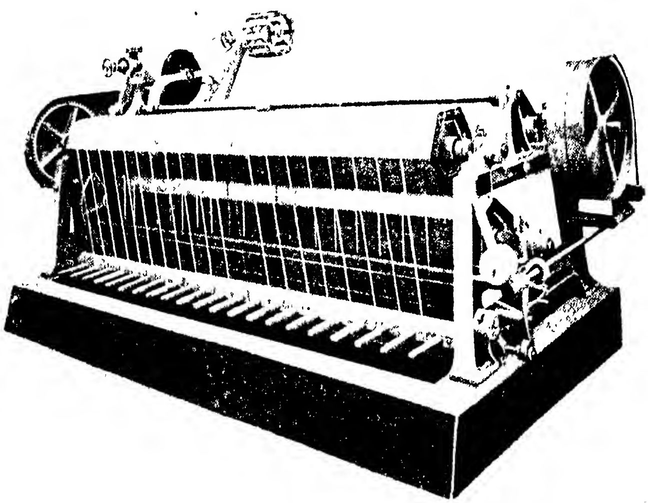


FIG. 166.—String Tub Washing Machine.

the case with chloride of lime. But we do not know of any practically successful process, even with electrolytic bleach liquors, where such high temperatures have been found of advantage. Schwalbe, in practical experiments on this subject, found a temperature of 85° F. to be the most suitable for bleaching, and Kind and Weindel through independent experiments on the stripping of indigo-dyed yarns came to the same conclusion.

Freiberger recommends a warm bleach in the continuous process of bleaching fabrics, where the latter are run through special apparatus containing the chemic and the goods are only in contact with the solution for a brief time. In this case a moderate heating of the hypochlorite bath increases the efficiency of the bleach. It is important, however, to regulate the strength of the bath by continual circulation

[5] *Ger. Pat.* 90,768.

and the addition of fresh chemic so that a constant chlorine content is maintained.

According to Erban[6] cop bleaching is carried out with chloride of lime solutions cooled with ice, in order to permit of the use of stronger chemics and a longer period of action without the danger of forming oxycellulose.

6. Effect of Light in Bleaching.

The effect of light has quite an important bearing on the results of bleaching as it increases the rate of decomposition of the hypochlorite

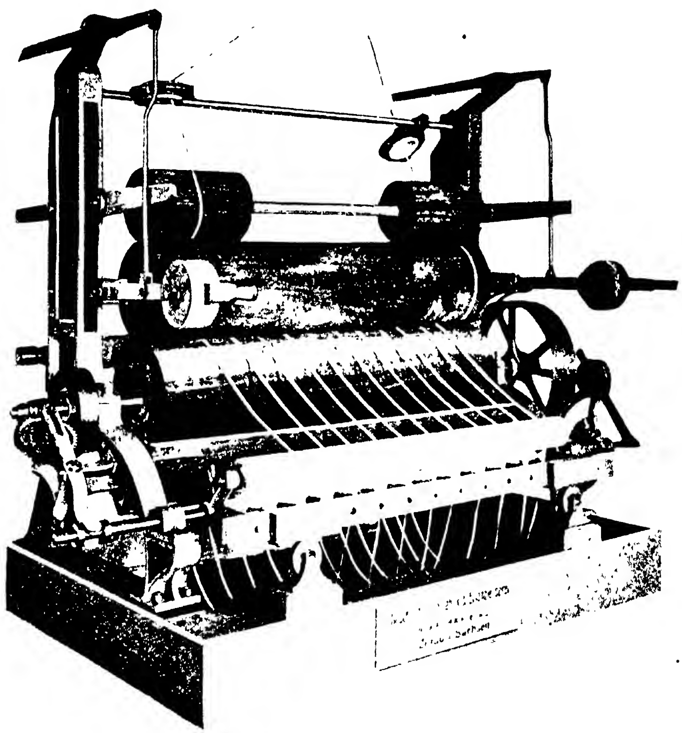


FIG. 167—Washer for Light Weight Fabrics.

solution. It has always been noticed that bleaching takes place more quickly when the goods after being chemicked are exposed to the action of sunlight. According to Keller[7] when goods saturated with hypochlorite solution are exposed to intense sunlight the formation of oxycellulose takes place, consequently it is recommended to cover the windows in bleacheries with yellow glass which will cut off the blue and

[6] *Chemiker Zeitung*, 1910, p. 1107.
[7] *Leipziger Färberzeitung*, 1909, p. 246.

violet rays, as these are the principal cause for the oxidizing action of the light. Sansone[8] also recommends the use of yellow glass. Kind,[9] however, from experiments conducted on this matter, disagrees with Keller as to the importance of the effect of light in causing the formation of oxycellulose. He believes that when the chemicked goods are exposed to strong direct sunlight there is local heating, and this together with the action of the carbon dioxide of the air may cause the severe oxidation leading to the formation of oxycellulose. While exposure to direct sunlight may cause untoward effects in bleaching, the present author is of the opinion that diffused sunlight is rather beneficial as an aid in bleaching, and there are seldom to be found bleacheries where the sunlight within and acting on the goods is so strong as to cause weakness through over-oxidation. Well-lighted bleacheries, where whitewash or white paint is liberally used so as to produce a maximum of diffused lighting effect, are much to be preferred to dark and ill-lighted rooms, and it will seldom be necessary to put yellow glass in the windows. If a lighting system permits of direct sunlight falling on the chemicked goods, the defect is easily remedied by the use of ground glass or other forms of glass causing proper diffusion of the light. Any evil effects in bleaching that may be caused by exposure of the goods to strong light are more liable to be due to local drying of the fiber so that it thus becomes overcharged with hypochlorite which, becoming highly concentrated through evaporation and in conjunction with the air, brings about the formation of oxycellulose and the consequent rotting of the fiber.

7. Souring or Treating with Acid.

The treatment with acid after steeping in chloride of lime is usually termed the "white sour." The method of operation is to pass the goods through a solution of sulfuric acid at about 1° Tw. cold, or a corresponding solution of hydrochloric acid, and the same machine is employed as that used for souring the goods after lime boiling. The acid has the effect of decomposing entirely any chloride of lime which may still be present in the material, and also of removing all lime compounds therefrom. In case sulfuric acid is used, finely divided sulfate of lime will be precipitated, which is subsequently removed from the goods by washing; if hydrochloric acid is used, however, the extremely soluble chloride of calcium is formed and no precipitation takes place. On this account, the use of hydrochloric acid is frequently recommended in place of sulfuric acid; but as the former is liable to be contaminated with iron, stains and spots are sometimes formed when it is used, so that the bleachers are more given to the use of sulfuric acid. Hydrochloric acid, however, may be obtained commercially, free from iron, and this may be used without fear of bad results.

If the goods, after treatment with the chloride of lime, have not been exposed to the action of the air or of mild acids, the full white bleach will not show up until after the souring. Sometimes, it is the

[8] *Zeugdruck*, p. 19.
[9] *Das Bleichen der Pflanzenfasern*, p. 139.

and the addition of fresh chemic so that a constant chlorine content is maintained.

According to Erban[6] cop bleaching is carried out with chloride of lime solutions cooled with ice, in order to permit of the use of stronger chemics and a longer period of action without the danger of forming oxycellulose.

6. Effect of Light in Bleaching.

The effect of light has quite an important bearing on the results of bleaching as it increases the rate of decomposition of the hypochlorite

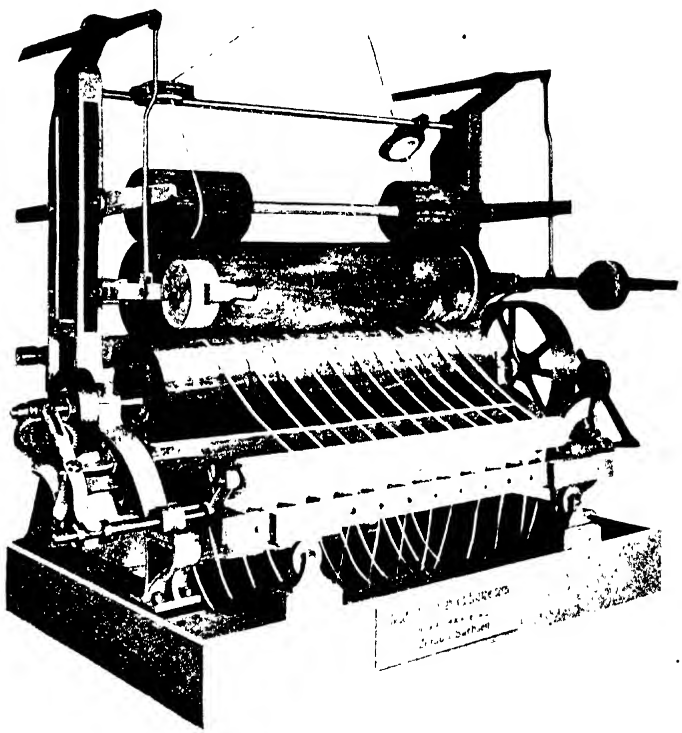


FIG. 167—Washer for Light Weight Fabrics.

solution. It has always been noticed that bleaching takes place more quickly when the goods after being chemicked are exposed to the action of sunlight. According to Keller[7] when goods saturated with hypochlorite solution are exposed to intense sunlight the formation of oxycellulose takes place, consequently it is recommended to cover the windows in bleacheries with yellow glass which will cut off the blue and

[6] *Chemiker Zeitung*, 1910, p. 1107.
[7] *Leipziger Färberzeitung*, 1909, p. 246.

liquors and the acid baths. After the final washing, which takes place in the usual form of machine, the goods, if intended to be marketed in the white form, are starched and tinted, and finally dried and calendered. If intended for dyeing or printing, the tinting and starching are omitted, and the goods are simply opened out, squeezed and dried over cans.

8. Effect of Acid Solutions on Cotton.

Cold dilute solutions of hydrochloric or sulfuric acid react with cotton, or cellulose in general, in a manner very similar to that of solutions of weak alkalies, forming compounds with the cotton without

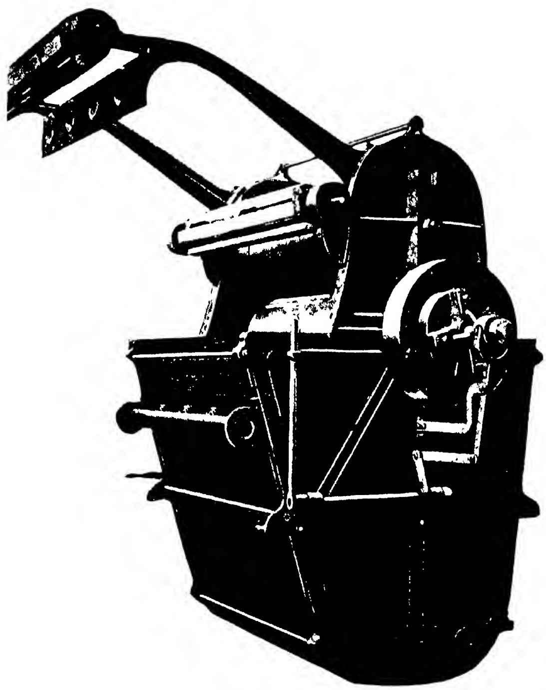


FIG. 169.—Dolly Washer (Text. Fin. Mchy. Co).

affecting the strength of the fiber. In concentrated solutions, however, either of these acids attack cotton very energetically, causing a destruction of the organic structure of the fiber, and forming a compound which has been variously called "hydrocellulose" and "hydracellulose," and which, more properly speaking, is probably a hydrate of cellulose. Hot solutions of the mineral acids, even when comparatively dilute, will rapidly attack cotton, and the rapidity of the reaction increases as the temperature and strength of the acid solution rise. Experience has

shown that in bleaching the temperature of the acid liquors employed should never exceed 70° to 80° F., and that the strength of the acid solutions should be below 2 percent, as otherwise there will be great danger of the cotton being tendered.

Acetic acid, on account of its not being injurious to vegetable fibers, and as its salts are very soluble, would be an excellent souring agent in bleaching were it not that it is much more expensive than sulfuric and hydrochloric acids. Oxalic acid could also be employed, but its lime salt is not soluble, and it is also too costly. As oxalic acid, however, is a good agent for the removal of iron stains, it is sometimes used in bleaching where the goods have received a yellowish tint through the use of ferruginous or iron-bearing waters. Oxalic and acetic acids are also sometimes employed as sours in bleaching fabrics containing woven colored yarns, as the stronger mineral acids would be liable to attack the dyes. Oxalic acid usually brightens blue colors, while acetic acid brightens black colors.

The strengths recommended for the acid liquors are as follows: for a hydrochloric acid sour after a lime boil use 5 gallons of acid per 1,000 gallons of water; for a sulfuric acid sour after chemicking, use 2 to 3 gallons of acid per 1,000 gallons of water; these figures are based on the fabrics being squeezed, for if they are impregnated with water, the acid will be too much diluted. In case the goods are not squeezed, the following proportions should be used: for hydrochloric acid sour after a lime boil, 10 to 12 gallons of acid per 1,000 gallons of water; for a sulfuric acid sour after chemic, 4 gallons of acid per 1,000 gallons of water. The figures in both the above cases are based on the supposition that the sours are heated to about 80° F. If the baths are used cold and the goods are not squeezed, the following proportions should be employed: for hydrochloric acid sour after a lime boil, 20 gallons of acid per 1,000 gallons of water; for sulfuric acid sour after chemic, 8 gallons of acid per 1,000 gallons of water. If a mixture of the two acids is used after a chemic, and the temperature of the bath be about 80° F., for unsqueezed goods the proportions should be 4 gallons of each acid per 1,000 gallons of water. If used cold, 8 gallons of sulfuric and 4 gallons of hydrochloric acid should be used per 1,000 gallons of water.

It has usually been supposed that solutions of hydrochloric acid are more readily removed from cotton by washing than corresponding solutions of sulfuric acid, but investigation has shown that this is not the case. While the lime compounds produced by the action of hydrochloric acid (calcium chloride) are very soluble and easily washed out as compared with the corresponding compounds produced by sulfuric acid (calcium sulfate), nevertheless the acid residues themselves are somewhat less easily removed in the case of hydrochloric acid. Koechlin as long ago as 1888 made some experiments on this matter; he steeped 100 grams of cotton yarn in 1500 c.c. of 1/5 normal sulfuric and hydrochloric acids respectively, centrifuged, and washed three times in 1500 c.c. of water. On testing the wash-waters the following proportions of the acids were found:

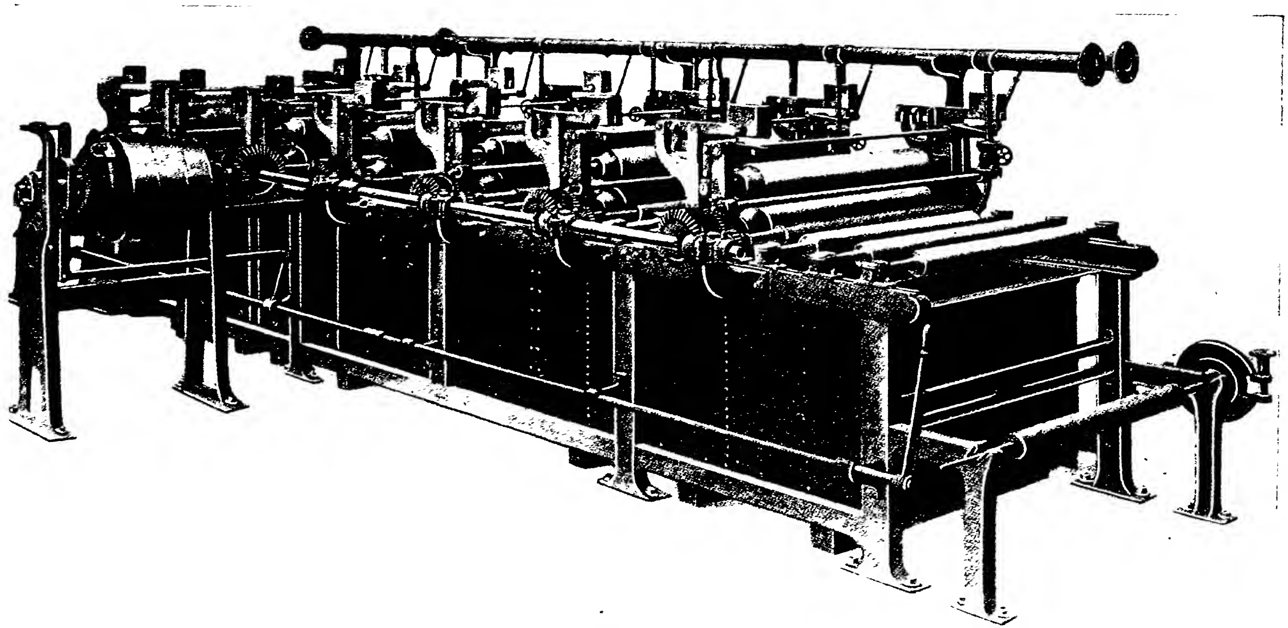


Fig. 170—Open Washing and Scouring Machine.

Wash-water	Hydrochloric acid	Sulfuric acid
1	3.7	3.6
2	0.9	0.5
3	0.2	0.1

It would seem, therefore, that hydrochloric acid is less readily washed out than sulfuric acid.[10]

From tests on the action of dilute sulfuric acid solutions on the tensile strength of cotton, Scheurer has shown that a solution containing 2 grams of sulfuric acid per liter at 80° C. has practically no deteriorating effect during the first half hour's treatment. At 90° C. the effect during the first half hour is, however, quite marked, amounting to a loss in strength of about 20 percent.

It is the drying of the acid solution in the cotton that produces the chief defects in bleaching traceable to the souring operation. In this case it makes little difference what the strength or temperature of the sour may be, for if acid residues are left in the goods and then dried, the acid liquor by evaporation of the water gradually becomes more and more concentrated until the cotton is seriously affected.

The weakening effect of dilute solutions of sulfuric acid on cotton also appears to be largely dependent on the duration of the action. Lang [11] gives the following tests in this connection:

Gms. Sulfuric Acid per liter	Percent Loss in Tensile Strength After						
	1 day	2 days	4 days	7 days	14 days	28 days	60 days
5	21	24	28	30	34	39	44
2	18	22	22	19	22	25	30
1	12	19	19	17	19	21	29

Holden [12] has shown that a proportion of sulfuric acid as low as 0.002 percent (on the weight of the cotton) when dried into the cotton fiber at a high temperature will cause serious deterioration in the tensile strength.

Organic acids have little or no deteriorating effect on cotton, even when dried into the fiber. Exception, however, may be made in the case of oxalic acid, which is sometimes employed by the cotton bleacher and laundryman for the removal of iron-rust spots from the cloth. The action in this case is supposed to be due to crystallization of the acid in drying within the cells of the fiber, thus causing their physical disruption. This view is preferred to that which holds that the oxalic acid has a chemical action similar to the mineral acids in causing a decomposition and breakdown of the cell tissue.[13]

Acid-rotting of cotton may be caused, not only by the action of acids themselves, but also by various salts which tend to hydrolyze and liberate free acid radicals. Many metallic salts are of this character, such as magnesium chloride, zinc chloride, alum, etc. This effect is especially noticeable when residues of solutions of these salts are dried

[10] *Mülhausener Berichte*, 1888, p. 547.
[11] *Elsässischer Textilblatt*, 1910, p. 635.
[12] *Jour. Soc. Dyers & Col.*, 1910.
[13] Kind, *Deutsche Farber-Zeitung*, 1909.

into cotton at elevated temperature such as experienced in drying machines and calenders.[14]

Apparently the chemical action of the acid or acid salts on cotton causing tendering or acid-rotting is to change the cellulose of the fiber into a body known as hydrocellulose, which is an intermediate product in the complete chemical breakdown of the cellulose to glucose, the

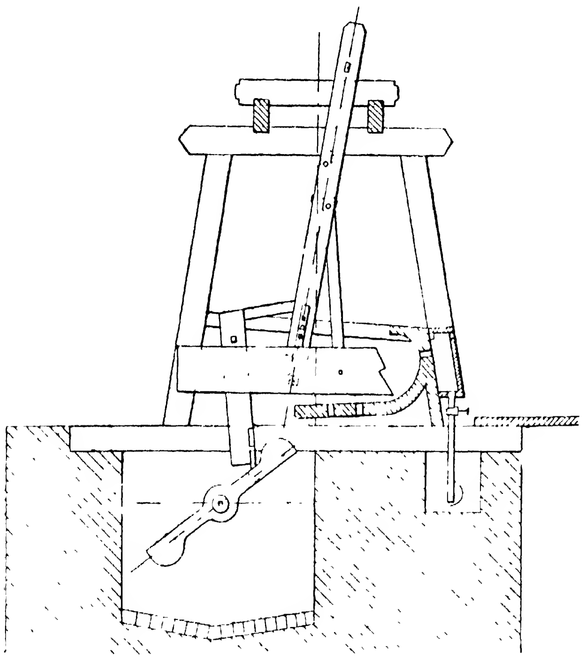


FIG. 171.—Wash Stocks.

latter being the final product in the action of the acid. Hydrocellulose differs from cellulose by being rather soluble in caustic soda solutions, and also on heating or on long exposure to the air, it develops a brown color. This accounts for the discolorations to be observed on acid spotted cloth after storing for some time.

9. Use of Antichlors.

By the term "antichlor" is meant a body that is capable of chemically neutralizing chlorine or hypochlorites to form neutral and harmless substances.

There are several compounds which may be used as antichlors in bleaching, as follows: (1) sodium bisulfite, (2) sodium thiosulfate (hyposulfite), (3) ammonia and (4) hydrogen peroxide. The first is

[14] Ristenpart, *Zeitsch, f. angew. Chemie*, 1912.

the one most largely used and it gives the best results, and is no doubt the cheapest in practice. Sodium thiosulfate is also cheap but is liable to precipitate sulfur on the goods which may afterwards lead to sulfur stains from contact with metals. Ammonia is quite effective but is more costly. Hydrogen peroxide is also more costly and besides it only neutralizes the active chlorine of hypochlorites and does not affect that of any chloramine which may be present. Also in using hydrogen

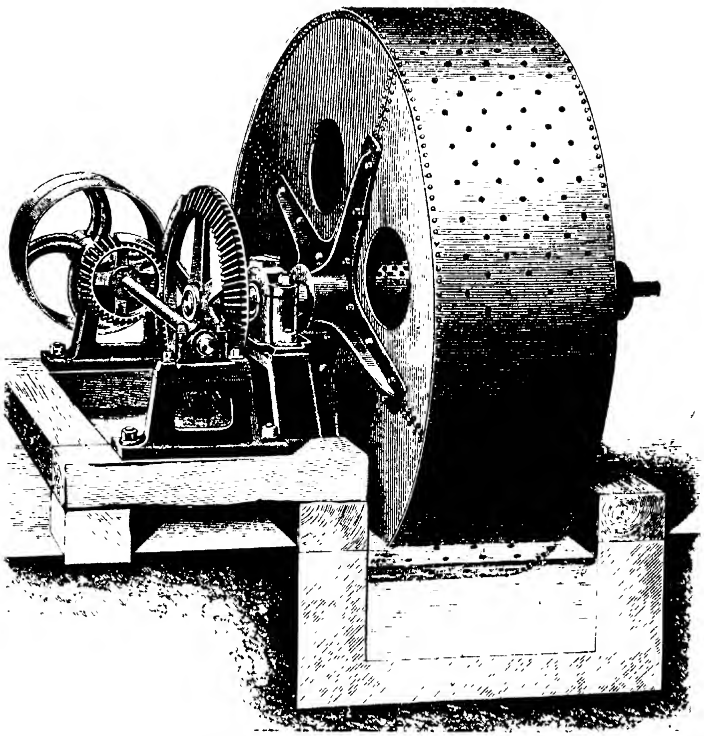


FIG. 172.—Wash Wheel.

peroxide as an antichlor it is not possible to use potassium iodide-starch paper to indicate the complete neutralization of the chlorine, since this test paper is also affected by hydrogen peroxide. In this case it is necessary, therefore, to use a solution of toluidine tartrate as the special reagent for chlorine.

10. Dry Bleaching.

In the process of "dry chloring" in calico printing, where the cloth is impregnated with a weak solution (0.2 to 1.0° Tw.) of chloride of lime and then without rinsing or souring is dried on hot drying

cans, one might expect that the fiber would be weakened and that oxycellulose would surely be formed. But such does not seem to be the case; Scheurer[15] has investigated this point and found that no appreciable weakening is to be noticed. It is no doubt probable that under the proper conditions of this process the hypochlorite is completely used up in performing its bleaching functions and there is no residue left to oxidize the fiber. Alkaline solutions of sodium hypo-

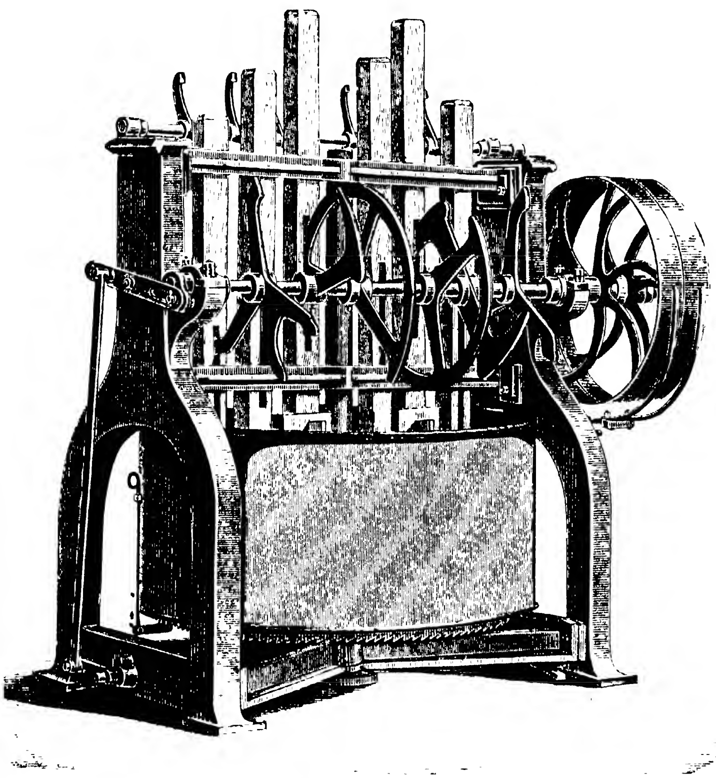


FIG. 173.—Circular Tom-Tom Washer.

chlorite cannot be used successfully with this process as the alkali will stain the goods and cause weakness; neutral solutions of sodium hypochlorite, however, may be employed with advantage.

With regard to the effect of drying and air in chemicked goods Witz describes the following interesting experiment: A strip of cotton cloth is hung in a solution of chloride of lime (5° Tw.) so that the greater part of the cloth is out of the liquor and so that the latter is

[15] *Mülhausener Berichte*, 1902.

drawn up through the fiber by capillary attraction; after treating thus for 1 hour the sample is rinsed and soured in a weak solution of sodium bisulfite. On testing the strength it will be found that that part of the cloth exposed to the air during the chemicking will be seriously weakened, and the presence of oxycellulose can readily be shown. This simple experiment emphasizes the need of caution during bleaching to keep the goods submerged beneath the chemic solution when a still bleach by soaking in the liquor is practiced.

11. **Cold Bleaching Methods.**

This manner of bleaching does not have reference to the use of cold bleach liquors, but to methods of bleaching in which the goods are not previously boiled-out with alkalies in a kier. Mention has already been made of this in previous sections relating to boiling-out.

Sometimes it is desirable to shorten the length of time required for bleaching. In certain cases where a three-quarter bleach is permissible it is possible to bleach without the use of chlorine, as, for instance, in the process of Hertel. Sansone also gives a process for "cold bleaching" especially applicable to raw cotton, the material without previous boiling-out being treated for 3 to 10 hours in sodium hypochlorite of 3 to 5° Tw. with the addition of excess of soda, then rinsing and treating with a bath of sodium bisulfite. If necessary, the operations are repeated to obtain the desired degree of bleaching. As might be expected, however, the use of a strongly alkaline hypochlorite is poor practice and does not give uniform results. According to Leblois, Piccni & Company,[16] cold bleaching may be carried out in a special apparatus in which raw cotton (or fine yarns) may be treated with cold liquors using a vacuum to obtain proper impregnation of the fiber and bleaching with "chlorogene." As it is difficult to purify the cotton without a boiling-out process in cold bleaching Bickel suggested the use of a pressure apparatus, using cold chloride of lime solution (2° Tw.) under about 2 atmospheres pressure for 3 to 4 hours and circulating with a pump. The further operations of rinsing and souring are also conducted under pressure. This method is particularly adapted to the bleaching of cops or other package goods such as beamed warps.[17]

Various methods of "cold bleaching" are practiced as circumstances suggest. In America large quantities of loose cotton are bleached in pack machines through which the necessary liquors may be circulated under pressure by pumping. A rinse with warm water is usually first given, and then cold chemic at 8° Tw. is circulated, followed by suitable rinses, souring and soaping. Such a method, of course, does not produce a very high degree of white, but it gives a cotton that may be spun into bleached yarns suitable for filling in colored fabrics. As the boiling-out is omitted, most of the wax is left on the fiber, so that it works quite well in spinning, and may be readily used for counts up to 60's.

[16] *Ger. Pat.* 36,962

[17] *Oesterreich Wollen und Leinenindustrie*, 1910, p. 1284.

There have been methods of bleaching suggested using a combination of hypochlorite liquor and soap solution, the idea being to combine a scouring and a bleaching action in one process. The method of Pick and Erban [18] is an example of this class. Various additions of this character have been suggested, such as Turkey-red oil, soap, castor oil soap, glycerin and alcohol, the latter for the purpose of increasing the capillarity of the solutions. It is probable, however, that solutions

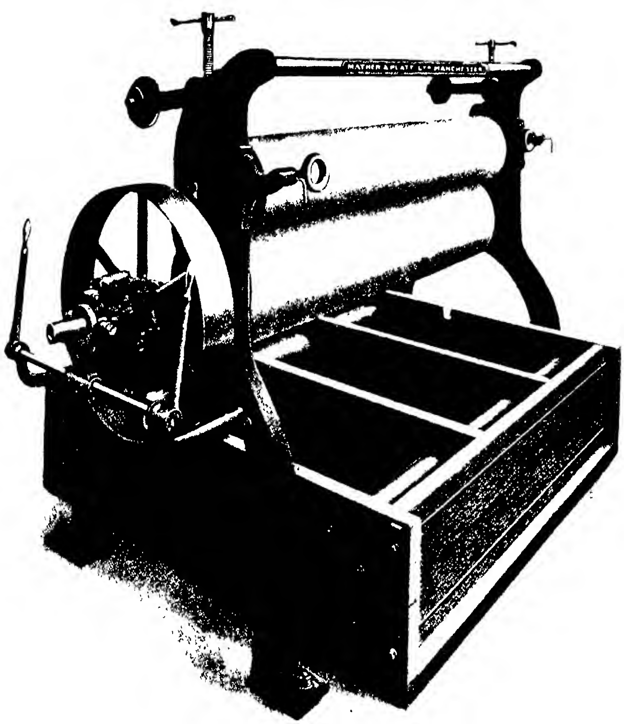


FIG. 174—Roller Washing Machine.

(bleaching or otherwise) penetrate the cotton fiber not so much through the action of capillarity as through that of diffusion or osmosis. Haller [19] has shown by microscopic investigation that the cotton fiber does not possess a porous structure and that the lumen or cell canal has little or no capillary effect. Herzog also has confirmed this fact as to the non-porous nature of the cotton fiber. The addition of Turkey-red oil or soaps cannot be made to chloride of lime liquors as an insoluble precipitate of lime soap is formed; consequently, when

[18] *Ger. Pat.* 176,609 and *Textil- und Farbereizeitung*, 1905.
[19] *Chem. Zeit.*, 1912, p. 169.

such oils or soaps are used as additions to the chemic it is necessary to use hypochlorite of sodium liquors. It might be thought that the methods of cold bleaching would be rather unsatisfactory in that they would not properly remove or destroy the motes and shives always present in cotton. To some degree this is true, but the results are often better than would be anticipated, as the bleach liquor discolors the shives to a pale yellow so they are not very apparent, and in the case of raw cotton, these foreign particles are usually so affected by the bleach solution as to be quite completely broken up and removed in the mechanical processing of the stock in the preparing, carding and spinning operations. Of course it cannot be expected that methods of cold bleaching will give a product comparable in purity of bleach and whiteness of color to that obtained by the usual processes of boiling-out and bleaching, and for a thorough bleach on cloth the cold method is not to be recommended; it must be limited to its legitimate uses in order to obtain satisfactory results.

Another cold bleaching process giving a partial bleach on cotton is that in which the goods are first steeped overnight in a solution of malt enzyme (Diax, Diastofor or Polyzime), then rinsed, soured and bleached in a cold chemic at 2° Tw.

Chapter XVIII.

The Bleaching of Cotton (*Cont.*).

1. Bleaching with Sodium Hypochlorite.

Sodium hypochlorite is extensively used for bleaching at the present time. This compound may be obtained by saturating a solution of caustic soda with chlorine gas, or by adding a solution of soda ash to one of chlorine of lime, whereupon calcium carbonate is precipitated and sodium hypochlorite is left in solution, or, further, by the electrolysis of a solution of sodium chloride. Chloride of soda, as this hypoclorite is called, is more expensive than chloride of lime, but its use is attended with less danger to the cotton, and hence it is sometimes used for fine goods. Sodium hypochlorite costs about twice as much as chloride of lime, but, on the other hand, its chlorine is twice as energetic in bleaching. Therefore, but little advantage in cost attends the use of sodium hypochlorite, except where a very soluble salt is needed, as when bleaching unspun cotton or fine yarns and goods.

2. Preparation of Sodium Hypochlorite.

Sodium hypochlorite, or chloride of soda, to maintain the analogy with chloride of lime, as prepared from bleaching powder may be made by a variety of means. The principal method, perhaps, is to mix together solutions of chloride of lime and soda ash, allow the precipitated carbonate of lime to settle, and draw off the clear liquor of "chloride of soda." In the preparation of sodium hypochlorite from soda ash and chloride of lime, care should be taken to have the final solution alkaline, and the soda ash should not contain much bicarbonate, as the presence of the latter body causes a rapid decomposition of the hypochlorite.[1] As there is always caustic lime present in solutions of bleaching

[1] According to Sunder the presence of 5 percent of bicarbonate in the soda ash will make the hypochlorite very unstable, the following experimental data being given for sodium hypochlorite solutions prepared by different methods:

Bleach with:	Cl gms. per liter	After 3 days	After 11 days
Soda ash cold	10 58	10 54	9.62
Soda ash 160° F.	11 01	10 65	9.90
With 5% $NaHCO_3$ cold	10 47	8 18	3.59
With 5% $NaHCO_3$ 160° F.	11 47	6 56	1.91

Holbing (*Fabrikation der Bleichmaterialien*) also gives the following data in this same connection:

	Clear Bleach Liquor ppt. with			Liquor and sludge ppt. with		
	Na_2CO_3	½ Na_2CO_3 ½ $NaHCO_3$	$NaHCO_3$	Na_2CO_3	½ Na_2CO_3 ½ $NaHCO_3$	$NaHCO_3$
Cl (gms. per liter)	15 07	8 5	10.28	17 73	18 08	12 97
After 1 day	14 89	6 27	7.90	17 73	15.60	9.38
After 3 days	13 83	4.60	5.10	17 73	8 62	6.13
After 5 days	11 16	2 38	2 87	17.73	5.74	3 72
Loss in percent	25 97	70 75	72.08	none	68.26	71.32

powder, there will consequently be a small amount of caustic soda formed in the above method. A good proportion of the ingredients to use is 60-65 lbs. of soda ash to 100 lbs. of bleaching powder, supposing the latter to be full strength (36 percent available chlorine). Sodium hypochlorite may also be made by the addition of caustic soda to a solution of bleaching powder; and still another method is the action of sodium sulfate on chloride of lime. The advantage of using the latter process is in the low price of sodium sulfate. There is precipitated in this reaction finely divided calcium sulfate which is very slow in settling; so in order to enhance the settling it is best to add some soda ash along with the sodium sulfate, whereby calcium carbonate is also formed, and this settles quite rapidly and at the same time serves to bring down the calcium sulfate.

Sodium hypochlorite in a solid form has been prepared by Bullier and Magnenne by compressing a mixture of chloride of lime and crystalline sodium sulfate in the dry state and without employing heat. A double decomposition takes place with the formation of sodium hypochlorite and calcium sulfate.

Higgins states that a very active solution of sodium hypochlorite may be prepared by precipitating a solution of bleaching powder with a mixture of soda ash and sodium bicarbonate. The function of the sodium bicarbonate is probably to unite with the free lime in the solution causing it to be precipitated and thus producing a very active bleaching liquor. Only a very small amount of sodium bicarbonate is needed.

In the preparation of sodium hypochlorite from bleaching powder and soda ash the following reaction takes place:

$$CaOCl_2 + Na_2CO_3 = NaOCl + NaCl + CaCO_3$$

The carbonate of lime is insoluble and settles out as a sludge or precipitate leaving a clear liquor consisting of a solution of sodium hypochlorite and sodium chloride, and thus quite free from lime compounds. Owing to the presence of caustic lime in the bleaching powder, there will also be a certain proportion of caustic soda in the liquor, and this will give it a distinctly alkaline reaction. As long as there is a deficiency of soda ash in the solution, the caustic soda that is formed will in turn react with the bleach to give sodium hypochlorite and calcium hydrate again:

$$Ca(OH)_2 + Na_2CO_3 = 2\ NaOH + CaCO_3$$
$$2\ NaOH + CaOCl_2 = Ca(OH)_2 + NaOCl + NaCl$$

The proportion of caustic soda in the solution will vary considerably with the method of mixing the liquors. When the soda ash solution is added directly to the entire mass of the bleaching powder, including both the liquor and the sludge, there will be a considerable amount of caustic soda formed in the reaction, as most of the calcium hydrate is in the sludge; but where only the clear liquor from the bleaching powder solution is used, as this contains only a small quantity of dissolved calcium hydrate, there will be only a relatively small amount of

caustic soda formed. In this connection Kind and Weindell[2] give the following experimental data: a clear bleaching powder liquor of a strength of 29 grams of available chlorine per liter which was treated with soda ash solution and diluted to a strength of 4 grams of available chlorine per liter showed an alkalinity corresponding to 0.028 gram of CaO per liter; whereas a milk of chloride of lime of a strength of 10.3 grams of available chlorine per liter on treatment with soda ash and dilution to a strength of 4 grams of available chlorine per liter gave an alkalinity corresponding to 0.168 gram of CaO per liter.

In the preparation of sodium hypochlorite liquor from the bleaching powder and soda ash there is always a certain loss of bleach liquor from the solution that remains with the sludge and which, therefore, cannot be utilized. The author has made the following test in this connection: 100 grams of fresh bleaching powder (41 percent available chlorine) were mixed with water (75° F.) and a solution of 65 grams of soda ash (56 percent Na_2O) was added. The liquor was made up to 2020 c.c. in a graduated glass cylinder with water and thoroughly mixed. After settling 1 hour there was 1600 c.c. of clear liquor, which only increased to 1660 c.c. after 14 hours settling. Consequently the sludge occupied about 14 percent of the total volume of the mixture. The density of the liquor was 7° Tw. and tested 20.25 grams of available chlorine per liter. The clear liquor (1660 c.c.) was drawn off and fresh water was added to original volume (2020 c.c.); after mixing and settling to 1660 c.c. again the clear liquor showed a strength of 3.4 grams of available chlorine. Therefore the total amount of bleaching value utilized by the clear sodium hypochlorite liquor was 1660 c.c. at 20.25 grams per liter = 33.615 grams Cl

1660 c.c. at 3.4 grams per liter = 5.644 grams Cl

Total = 39.259 grams Cl

or 95.7 percent of the available chlorine in the original bleaching powder, leaving 4.3 percent as loss in the sludge.

3. Various Hypochlorite Preparations.

Chlorozone was a preparation of sodium hypochlorite first put on the market by Brochoki.[3] It is obtained by saturating a sold solution of caustic soda with chlorine gas, which is claimed to be previously peroxidized (?). It occurs as a clear limpid liquid of a density of from 1.18 to 1.250. Chlorozone of the latter strength contains the following:

	Percent
Chlorine	12.68
Oxygen	5.82
Sodium	8.62
Water of combination	3.38
Water of solution, etc.	69.50

[2] *Leipziger Monatschrift fur Textilindustrie*, 1908

[3] Chlorozone was a preparation which contained free hypochlorous acid, and its value was at first rather deceiving on account of its increased bleaching energy, but owing to this fact it was liable to form oxycellulose and this limited its general acceptance in the trade. The bleacher himself can produce a similar chemic by carefully neutralizing ordinary hypochlorite solution with acid.

Chlorozone forms a very safe bleaching liquor, and may be used both hot and cold. Weight for weight it has three times less chlorine than bleaching powder, and on account of its relatively high price, it is not much used. It is probably that chlorozone contains oxy-chlorine compounds, and hence it is different from plain sodium hypochlorite of soda. Solutions of chlorozone also keep better than the latter. A somewhat similar product is that known as *chlorogene*.

Hypochlorite of potash may be prepared and used in a similar manner to the corresponding soda salt, but as the potash compound is dearer it is never used. Cotelle's hypochlorite is a specially prepared hypochlorite of soda made by the sodium sulfate method. It is manufactured in France by a secret process, and the product is almost neutral, containing neither caustic nor carbonated alkali, on which account it is highly esteemed for the bleaching of fabrics containing colored yarns; it may also be employed for the bleaching of silk.

Hypochlorite of magnesia is prepared by mixing solutions of magnesium sulfate and chloride of lime; the solution so obtained is quite neutral and its bleaching power is good. The solutions decompose very quickly, however, and so it does not serve as well as solutions of sodium hypochlorite. Hypochlorite of zinc may be prepared by mixing solutions of zinc sulfate and chloride of lime. Its bleaching action is very good, but it is liable to weaken the fiber.

In order to remove the excess of lime or soda from solutions of chloride of lime or sodium hypochlorite, the addition of a solution of magnesium chloride is recommended. In the case of chloride of lime, the following reaction takes place:

$$CaO + MgCl_2 = CaCl_2 + MgO$$

The magnesia, being insoluble, is precipitated, while the calcium chloride remains in solution. In the case of sodium hypochlorite or other akaline bleach liquor, a similar reaction takes place. Magnesium chloride thus used in connection with chloride of soda very materially increases its bleaching activity, by neutralizing the excess of alkali present, and furthermore it prevents the injurious action on the fiber due to the presence of the lime in the solution.

"Wilson's Liquor" is the name given to a solution of aluminium hypochlorite. It is said to be a very effective bleaching agent, and is prepared by adding a solution of aluminium sulfate to one of bleaching powder. It may also be prepared, and perhaps more economically, by the action of chlorine on sodium aluminate, the latter being the method proposed by Weise. By the use of aluminium bleaching liquors the action appears to be more rapid, while the use of acid is not required, and hence there is less danger of tendering the goods.

Bregeard has recommended the addition of zinc sulfate to sodium hypochlorite solution for the purpose of increasing its bleaching action There have also been methods suggested for combining the action of hypochlorite solutions with hydrogen peroxide, ozone, and other oxidizing agents; these, however, have never amounted to anything of practical value.

Hertel has published the result of certain experiments made by him on the use of hypochlorous acid gas for the bleaching of cotton yarn. He obtained the gas by decomposing bleaching powder with dilute sulfuric acid, and the gas so evolved was allowed to react on the cotton yarn, which had previously been well scoured and washed, and was placed while still wet in a closed vessel in contact with the gas. The bleaching action is said to have proceeded very rapidly and effectively, but the process does not appear to have met with any success on a large scale.

4. Use of Liquid Chlorine.

One of the chief methods employed at the present time for the preparation of sodium hypochlorite bleach liquors is by the use of liquid chlorine reacting with a solution of caustic soda or soda ash. The earliest method of preparing the hypochlorite bleach, in fact, was the solution of chlorine gas in caustic soda solution, the chlorine gas being obtained by the old process of the action of hydrochloric acid on manganese dioxide. The bleacher himself in the old days prepared his own chlorine gas and made his own bleach liquor. The intro-

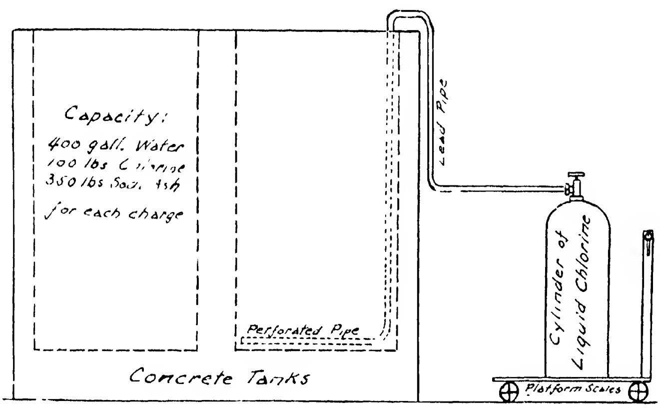


FIG. 175.—Diagram of Liquid Chlorine Installation for Preparation of Sodium Hypochlorite Bleach Liquor.

duction of bleaching powder, however, soon caused the chlorine gas process to fall into disuse, as the latter was more expensive (on account of the manganese dioxide required) and was also a disagreeable process to conduct. The modern methods of preparing chlorine gas by electrolysis, however, have made it possible to readily obtain this gas in the liquefied form, which may be easily transported in steel cylinders, and thus furnishes a convenient and relatively cheap method of using chlorine for the preparation of hypochlorite bleach liquors. The liquefied chlorine gas is at present well known in trade and is

usually put up in heavy metal cylinders containing about 100 to 150 lbs. of the gas, though at times larger cylinders containing 2000 lbs. are also used. Under these conditions the gas is held in the container as a liquid under a pressure of about 90 lbs. (at the ordinary temperature of 70° F.). The container is provided with a suitable valve (usually of copper) which properly regulates the flow of the chlorine gas from the cylinder. As the chlorine in the container is absolutely dry it does not attack the metal of either the cylinder or the valve, but if moisture is allowed to enter the cylinder (by sucking back of the liquid, for example, into an exhausted cylinder still left connected with the solution) the metal parts will be rapidly corroded, so care must be had not to allow water to enter the chlorine container.

Liquid chlorine is now manufactured on a very large scale both in Europe and America by the electrolysis of a saturated solution of common salt. An electric current of low potential is employed and the salt is decomposed into sodium at the cathode and chlorine at the anode. Unless a special form of cell is used whereby the metallic sodium itself is produced, as fast as this metal is set free in the cell it reacts with water to form sodium hydroxide. The chlorine gas is drawn off from the anode and is carried through a series of processes for purifying and drying it, after which it is passed through compressing and refrigerating machinery which converts it into the liquid form, in which state it is pumped into suitable containers for shipment. Chlorine gas in order to be liquefied must first be purified to a very high degree, consequently the liquid chlorine of commerce consists of practically chemically pure chlorine, its chemical analysis being about as follows:

	Percent
Chlorine	99.80—99.99
Carbon dioxide	0.01— 0.20
Oxygen and air	0.00— 0.10

When employed for bleaching purposes the chlorine is dissolved in an alkaline liquor (either caustic soda or soda ash) with the resultant formation of a solution of sodium hypochlorite. When caustic soda is used for the solution the reaction is as follows:

$$2\ NaOH + 2\ Cl = NaOCl + NaCl + H_2O.$$

In the preparation of this solution it should always be mantained alkaline, that is to say, the caustic soda should always be in slight excess, as otherwise free hypochlorous acid would be formed in the solution which would make it quite unstable. The solution of chlorine in caustic soda also liberates considerable heat, and care must be taken not to allow the solution to become heated up to any extent (it should be kept below 80° F.). This is accomplished by either introducing the chlorine very slowly or by the use of ice or other methods of refrigeration. If the solution becomes hot there will be secondary reactions taking place, resulting in the formation of sodium chlorate:

$$3\ NaOCl = 2\ NaCl + NaClO_3$$

and this considerably lowers the strength of the solution and decreases its bleaching efficiency.

If excess of chlorine is added to the caustic soda solution free hypochlorous acid will be formed and the solution will actually become acid in character. Under these conditions the solution acts with rapidity in bleaching, but, on the other hand, its stability is very low; that is to say, its strength in terms of available chlorine rapidly decreases on standing, and consequently there is a considerable loss of chlorine value.

5. **Preparation of Hypochlorite from Liquid Chlorine.**

In absorbing chlorine gas in a solution of caustic soda to full saturation of the alkali there would be required 40 parts of caustic soda (actual NaOH) for 35.5 parts of chlorine. Using commercial caustic soda would require about 125 lbs. for 100 lbs. of chlorine, which would allow for a slight excess of alkali in the solution. The use of too great an excess of alkali is not advisable, as this reduces the activity of the solution, and the bleaching takes place very slowly. Also the use of strongly alkaline bleach liquors is liable to cause stains on the cotton; it is also rather difficult to remove the excess of alkali from the fiber by washing and the use of considerable acid wash waters must be resorted to, and this is liable to introduce defects. The bad effect of the alkaline bleach liquor is especially noticeable when the saturated goods are exposed to the air for any length of time, as this will nearly always cause the formation of brown alkali spots and the possible tendering of the goods.

According to the Deutsche Solvay Werke (*Eng. Pat.* 21,411 of 1910), when chlorine is dissolved in an alkaline liquor consisting of a mixture of caustic soda and soda ash, the gas first acts in accordance with the equation:

$$2\ NaOH + Cl_2 = NaOCl + NaCl + H_2O,$$

When the whole of the caustic soda has been converted, the chlorine next attacks the carbonate in the following manner:

$$Na_2CO_3 + Cl_2 + H_2O = NaCl + NaHCO_3 + HOCl.$$

The proportions of hypochlorous acid and sodium hypochlorite in the final liquor can therefore be varied at will by adjusting the relative quantities of caustic soda and soda ash. The yield of available chlorine in this way is said to be much greater than when the chlorine gas is separately dissolved in the alkaline solutions and then the latter mixed, while the stability of the liquor (even when the proportion of free hypochlorous acid is considerable) is much better than that of an electrolytic chemic. The following proportions are recommended for the preparation of the sodium hypochlorite solution: 50 lbs. of chlorine are passed in slowly (in order to avoid strong heating) to 400 gallons of a solution containing 34.2 lbs. of caustic soda and 41.6 lbs. of soda ash, the liquor being well stirred during the operation. The chemic thus obtained contains 16.35 grams of available chlorine per liter, of which

60 percent is in the form of sodium hypochlorite and 40 percent as hypochlorous acid.

The concentration of the caustic soda solution used for absorbing the chlorine gas has considerable bearing on the proper preparation of the liquor. If the solution is quite dilute the gas will absorb poorly and chlorine fumes will escape into the air, causing loss of gas and

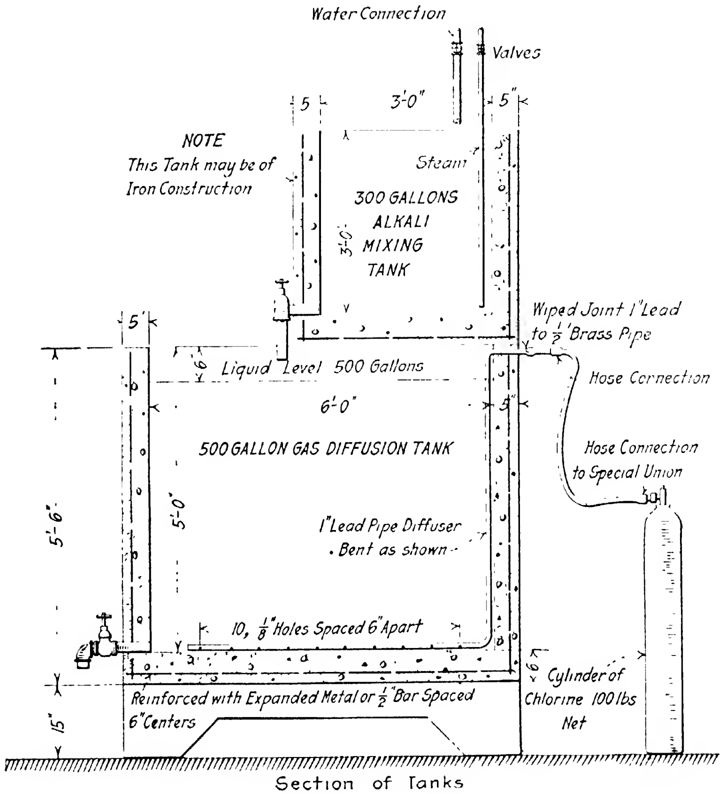


FIG. 176.—Large Scale Equipment for Liquid Chlorine Bleaching.

also resulting in a very obnoxious and disagreeable condition for the workmen. A good strength of solution to employ is 400-500 gallons of water, 125 lbs. of caustic soda and 100 lbs. of chlorine. The use of very strong caustic liquors will cause the solution to heat up too much. In absorbing the chlorine gas it should be passed into the solution through a lead pipe perforated at the bottom and the liquor should be contained in a deep narrow tank so as to allow the gas to pass through as much liquor as possible. If the layer of liquor is too shal-

low the gas will have to be run in very slowly in order to obtain good absorption. Special forms of absorbers may be used, such as porous filter stones which break up the gas into very fine globules, or better yet where compressed air is available, the chlorine gas may be mixed with air when introduced into the caustic liquor, and as this greatly increases the absorption surface the gas is dissolved quite rapidly and no excess fumes escape from the surface of the solution. The tower method of absorption may also be used, the chlorine gas being introduced at the bottom of a tower or column which is filled with coke, porous stone or cups through which the caustic soda solution passes. This method is especially suited where it is desired to continuously prepare a dilute solution of bleach liquor from a weak caustic liquor. This method may also be used advantageously for the preparation of dilute solutions of hypochlorous acid, either using plain water as the absorbing medium or a very dilute solution of caustic soda and oversaturating with chlorine gas. Such liquors may be used at times in the bleaching of raw cotton or paper pulp in machines where it is desired to have a rapid bleaching effect and no alkali present.

Instead of employing caustic soda for the preparation of the hypochlorite liquor, a solution of soda ash may be used. Under many circumstances this has certain advantages. When a solution of soda ash is used for absorbing the chlorine, the solution of the gas is rapid and complete; there is no tendency for fumes to escape from the surface of the liquor due to incomplete absorption. Also the liquor does not heat up and therefore the gas may be passed into the solution much more rapidly than with the use of caustic soda, and no outside cooling is required. Furthermore, the solution does not contain any excess of caustic soda. On the other hand, a much larger proportion of alkali must be used in preparing this liquor owing to the fact that in the reaction between chlorine and sodium carbonate in addition to sodium hypochlorite there is also formed sodium bicarbonate, and the further action of chlorine on this would result in the formation of hypochlorous acid and the entire solution then becomes so unstable that it rapidly starts to decompose, often with such velocity as to effervesce violently. In order to obtain a solution of sufficient stability for bleaching purposes it is necessary to use 3-3½ parts of soda ash to 1 part of chlorine. The reactions involved may be considered to be as follows:

$$2\,Na_2CO_3 + Cl_2 + H_2O = NaCl + NaOCl + 2\,NaHCO_3$$

that is to say, 71 parts of chlorine will require 212 parts of actual sodium carbonate or 1 of chlorine to 3 of alkali, and in using commercial soda ash it is safer to use 3¼ to 3½ parts of alkali.

If the introduction of chlorine is continued beyond the point indicated by the above equation, the sodium bicarbonate will be acted on with the formation of carbonic acid and hypochlorous acid:

$$NaHCO_3 + Cl_2 = NaCl + CO_2 + HOCl$$

and apparently under the influence of the carbonic acid the hypochlorous acid breaks up into oxygen and hydrochloric acid, and the latter acid continues the reaction with increasing violence.

The reaction between soda ash and chlorine has been described as:

$$Na_2CO_3 + Cl_2 + H_2O = NaCl + NaHCO_3 + HOCl$$

but according to this equation 1 part of chlorine would require only 1½ parts of soda ash, and under the ordinary conditions of temperature and concentration of solutions, the present author has never found it possible to prepare a hypochlorite liquor with those proportions, as the solution decomposes with much effervescence long before these proportions are reached. In practice, where this form of hypochlorite solution is used for actual bleaching operations, the following proportions are used:

400-500 gallons water
325-350 lbs. soda ash
100 lbs. chlorine

It is also possible to use a mixture of caustic soda and soda ash for the purpose of absorbing the chlorine; a suitable proportion is:

400-500 gallons water
150-200 lbs. soda ash
80 lbs. caustic soda
100 lbs. chlorine

The sodium hypochlorite solution prepared with caustic soda is more stable than that with soda ash. The former if preserved in suitable tanks and not exposed unduly to light and air will lose its chlorine strength very slowly, whereas the strength of the latter will run down more rapidly. On this account when used in practice it is best to prepare the hypochlorite bleach just before using in order to obtain the full efficiency of the chlorine. The instability of the soda ash hypochlorite liquor is caused by the presence of the relatively large amount of sodium bicarbonate.

The use of liquid chlorine in the preparation of sodium hypochlorite bleach liquors has become very extensive in the United States during recent years. It appeals to the bleacher on account of its neatness and cleanliness of operation, its freedom from the many disagreeable features associated with the use of bleaching powder, and also by the fact that there is no bulky and obnoxious sludge to get rid of. The preparation of the bleach liquor is also under ready control and can be made up as needed to coördinate with the other processes of the bleaching operations. It also has the same advantages of the use of any form of sodium hypochlorite in that it is less injurious to fabrics, gives a softer bleach free from lime compounds, and eliminates many of the objectionable features of the lime bleach.

Owing to the wide use of liquid chlorine in bleaching, the properties of this substance and of the gas will be found of considerable interest. The gas is of a greenish yellow color and has a pungent and characteristic odor. It is highly irritating to the mucous membranes of the eyes, throat and nose, and produces extreme coughing and great inflammation if allowed to act for any length of time or in any quantity. It also has a poisonous action on the system, and becomes very danger-

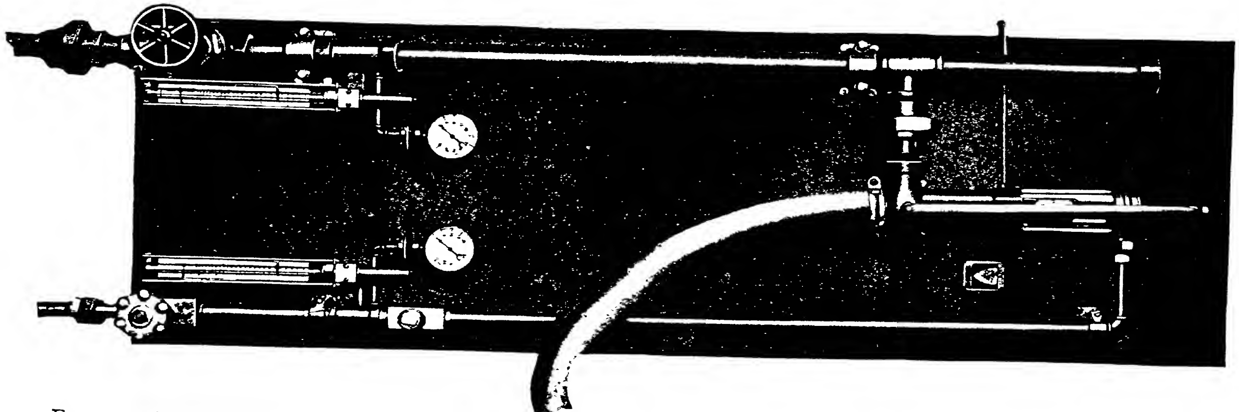


FIG. 177.—Special Control Equipment for Making Bleach Liquors from Liquefied Chlorine (Wallace & Tiernan).

ous if inhaled into the lungs. A very small proportion of the gas mixed with air will make the conditions of breathing not only very disagreeable but also dangerous. The specific gravity of chlorine gas is 2.49 (air = 1) and its atomic weight is 35.45. It is liquefied at 0° C. under a pressure of 6 atmospheres, and forms a clear yellow liquid with a specific gravity of 1.44. When confined within containers liquid chlorine will indicate a pressure (above that of the atmosphere) varying with the temperature; at —33.6° C. (—28° F.) the pressure is zero, at 0° C. (32° F.) the pressure is about 37 lbs., at 10° C. (50° F.) the pressure is about 56 lbs., at 20° C. (68° F.) the pressure is about 80 lbs., at 40° C. (104° F.) the pressure is about 220 lbs., and at 100° C. (212° F.) the pressure is nearly 600 lbs. per sq. in.

The installation required for the preparation of sodium hypochlorite from liquid chlorine is comparatively simple. The cylinder or tank containing the chlorine is placed on a platform scales, the valve is suitably connected with a lead pipe which passes into the alkaline solution contained in a wooden or cement tank, the latter being preferable. It is wise to have the lead conduit pipe for the chlorine gas to rise in a bend to some height above the solution to prevent the liquid from being drawn up through the pipe when the flow of chlorine becomes exhausted. The chlorine gas is run into the alkaline solution until the desired weight of chlorine (as shown by the loss in weight on the scales) is used. Where cylinders containing 100 lbs. of chlorine are used and the entire amount is to be employed in one batch, the connections may be made, the valves opened and the gas allowed to run out all night into the alkali, so that the solution is all ready for use the following morning. As the different cylinders of chlorine, however, will show quite some variation in the amount of gas they contain, when this method is used, it is best to first ascertain the quantity of chlorine in the cylinder and then make up the desired alkali solution on the basis of the proportions given in the foregoing pages. When the chlorine gas is run from the cylinder rather rapidly the latter will become chilled by the rapid evaporation and in a moist atmosphere ice will form on the outside of the container. This chilling will materially reduce the rate of flow of the gas, which, however, may be increased if desired by standing the cylinder in a tub or tank of hot water.

A measuring device for feeding in any definite quantity of chlorine gas to a solution has been constructed and adapted to the use of liquid chlorine in bleaching. By its use a very nice control may be had over the flow of the gas in the preparation of hypochlorite solutions (see Figure 177).

The solution of sodium hypochlorite prepared from liquid chlorine is employed in bleaching just as any other chemic solution. If prepared in the manner as described above when used in comparison with solutions of bleaching powder it should be employed at about one-half the strength of the latter to obtain the same bleaching effect; that is to say, if the bleaching powder chemic has been used at about 2° Tw., corresponding to about 5.6 grams of available chlorine per liter, the

sodium hypochlorite solution should be used at a strength of about 2.8 grams of available chlorine per liter. For most purposes of bleaching it will require about 1 to 2 lbs. of liquid chlorine to bleach 100 lbs. of cotton goods; raw stock will require about 1½ to 2½ lbs., and low grade underwear yarns may require as much as 3 lbs.

6. Electrolytic Bleach Liquors.

When an electric current of proper strength is passed through a solution of sodium chloride (common salt) a certain amount of sodium hypochlorite is formed.[4] A large excess of sodium chloride also remains in solution. Such a liquor has been employed quite successfully for bleaching. In theory the process of preparing solutions of hypochlorites electrolytically has always been inviting, and a great deal of experimental work has been done on the problem. A number of different chlorides have been used for electrolysis, such as sodium chloride, magnesium chloride, calcium chloride, and mixtures of these salts. Various types of electrolyzers have been devised with more or less success in the overcoming of certain obstacles in the way of economical operation.[5] It has generally been found in practice, however, that the cost of electrolytic hypochlorite liquors is always greater than that anticipated by theory, there evidently being a great loss of electrical energy which cannot be utilized properly in the bath.[6]

According to most experimenters the solution of hypochlorite of soda prepared electrolytically has a higher bleaching efficiency than a solution of chloride of lime containing an equivalent amount of available chlorine. The same observation, however, is also true of sodium hypochlorite solutions prepared either by interaction of soda ash and bleaching powder or by the action of chlorine gas (liquid chlorine) on solutions of caustic soda or soda ash. The consensus of opinion seems to be that the sodium hypochlorite solutions are about twice as efficient as those of chloride of lime.

When an electric current is passed through a solution of common salt the salt is decomposed into its elements or "ions," thus:

$$NaCl = Na + Cl$$

The sodium is liberated at the cathode and the chlorine at the anode of the cell. If the cell is a simple one without a diaphragm to separate

[4] Brand in 1820 first showed that cotton cloth could be bleached in an electrolyzed salt solution. It was not until 1883, however, that this process was seriously investigated for the first time at the University of Glasgow

[5] As the electromotive force necessary to decompose sodium chloride is 4.2 volts, and under this tension one ampere disengages in one hour 1.331 gms. of chlorine or 0.420 liter of gaseous chlorine, there is theoretically required one horse-power to liberate in one hour 232.92 gms of chlorine or 73.5 liters. In practice, however, this theoretical result can never be reached, owing to many side considerations

[6] The principal source of waste in the current is probably due to the reduction of the hypochlorites at the cathode. According to a recent German patent, this waste may be avoided to a great extent by using salts of alkalies and alkaline earths together (sodium and magnesium chlorides) and adding an alkaline solution of rosin to the electrolyte The following example is given for the electrolyte: 14 liters of a 10 percent solution of common salt containing 40 gms. of calcium chloride, 30 gms of lime, and 50 cc. of a concentrated solution of rosin in soda ash This mixture is electrolyzed with a current of 125 amperes, and the yield in 1 hour is said to be 9 gms of active chlorine per liter The rate of production of the chlorine then falls off to 17 gms in 2 hours, 23 gms in 3 hours, 28 gms. in 4 hours and 33.5 gms. in 6 hours.

the two electrodes, secondary reactions immediately take place. The sodium reacts with the surrounding water forming caustic soda and liberating hydrogen gas:

$$Na + H_2O = NaOH + H$$

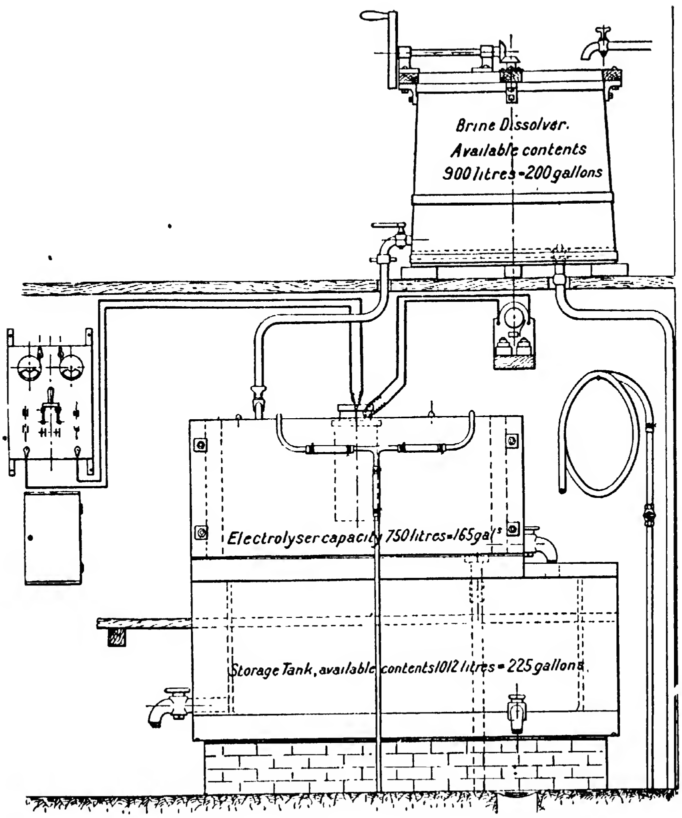


FIG. 178.—Diagram of Plant for Electrolytic Bleaching.

The chlorine next reacts with the caustic soda forming sodium hypochlorite, sodium chloride, and water.[7]

$$Cl_2 + 2\,NaOH = NaOCl + NaCl + H_2O$$

The final result of the electrolysis, therefore, is that hydrogen gas is liberated at the cathode and sodium hypochlorite is found in the solution. The electrolytic bleach liquor, therefore, consists of a mixed solution of sodium hypochlorite and common salt.

[7] In the practical operation of the electrolytic cell there is always some chlorine liberated, consequently, the electrolytic bleach liquor produced is always slightly alkaline.

Besides the reactions above indicated there are also some other more complicated ones taking place in the cell during its operation. In the first place the liberated hydrogen acts on the hypochlorite in some degree, forming common salt and water:

$$NaOCl + H_2 = NaCl + H_2O$$

In the second place, the current acts on some of the sodium hypochlorite as it accumulates in solution, causing an electrolysis of this salt in the same manner as with the common salt, breaking it up into the following ions:

$$Na\,O\,Cl = Na + O\,Cl$$

The latter ion, being discharged at the anode, reacts with the surrounding water in two ways, forming hypochlorous and chloric acids:

$$2\,O\,Cl + H_2O = 2\,H\,O\,Cl + O$$
$$6\,O\,Cl + 3H_2O = 2\,Cl\,O_3 + 4\,Cl + 6H + 3\,O$$

Consequently there is a mixture of oxygen, hydrogen, and chlorine liberated at the anode. Some of the hydrogen will combine with the chlorine forming hydrochloric acid, while the oxygen escapes. A third secondary reaction is oxidation of some of the hypochlorite to chlorate, as follows:

$$Na\,O\,Cl + 2\,HO\,Cl = Na\,Cl\,O_3 + H\,Cl$$

Furthermore, the hydrochloric acid formed in this reaction, as well as in the preceding one, reacts with the hypochlorite, converting it back to common salt, as follows:

$$Na\,Cl\,O + H\,Cl = NaCl + HOCl$$

At the anode the freshly liberated chlorine before it has had an opportunity to combine with the caustic soda from the other pole will react to some extent with the surrounding water, giving hydrochloric acid and oxygen:

$$Cl_2 + H_2O = 2\,HCl + O$$

As already shown above, both the hydrochloric acid and the oxygen cause secondary reactions again to take place.

7. Conditions of Electrolysis.

A number of conditions influence these reactions, among which are the temperature of the solution and the current density. The alkalinity of the liquor is also an important factor.[8] In general practice electrolytic hypochlorite liquors are nearly always slightly alkaline, caused by the fact that a portion of the chlorine liberated at the anode is used up in secondary reactions or escapes into the air; this leaves a part of the caustic soda unneutralized in the solution. The more alkaline the solution becomes the greater will be its stability and the less rapid its bleaching action.

[8] According to Ahlin (*Papier-Zeit.*, [illegible], p. 834), the alkalinity of electrolytic bleach liquors should be such that 1000 c.c. of the solution when reddened with phenolphthalein is decolorized by the addition of 2 drops of normal acid. Before being employed for bleaching the alkalinity should be neutralized.

Another disturbing factor in the operation of the hypochlorite cell is the rise in temperature of the solution caused by the heat generated by the passage of the electric current. This heat not only represents loss of energy or current but also causes a complication in the secondary chemical reactions. High temperatures, for instance, favor the direct formation of chlorates in the reaction of chlorine on caustic

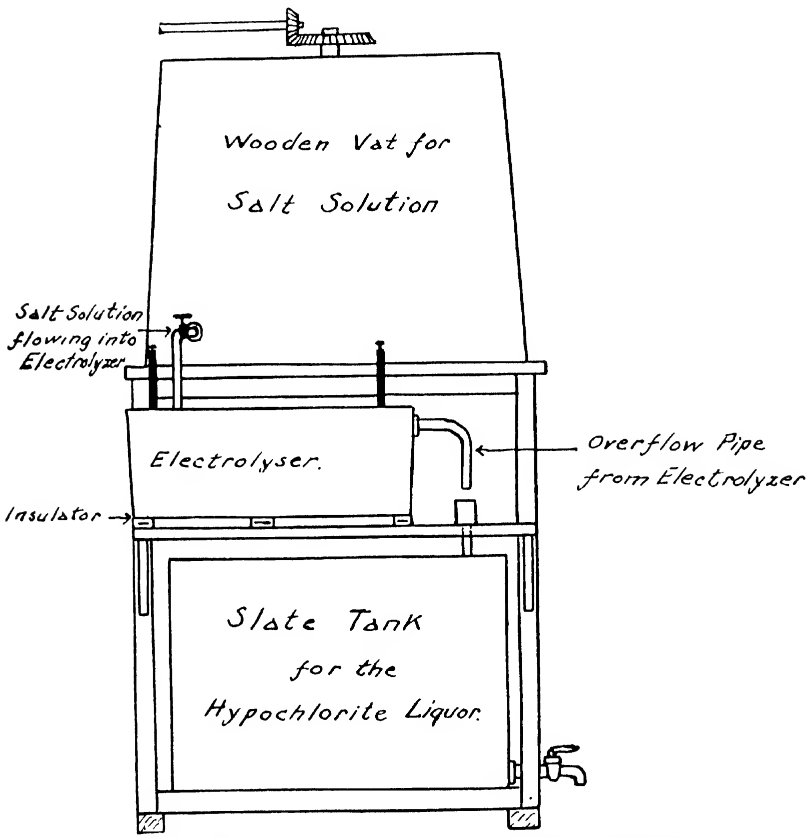


FIG. 179.—Diagram Showing Arrangement of Oettel Electrolyzer.

soda.[9] Imperfect circulation of the liquor in the electrolyzer also favors the formation of chlorates. In some forms of electrolyzers the temperature is kept down by cooling with a coil of pipe through which cold water is kept circulating. Excessive cooling, however, should be avoided as this reduces the conductivity of the electrolyte; the best temperature to maintain is between 95-100° Fahr.

[9] The direct formation of chlorate may be represented by:

$$NaCl + 3\ H_2O = NaClO_3 + 3\ H_2$$

The current density also affects the secondary reactions taking place; a high current density at the cathode lessens the amount of reduction taking place. Generally high current density at both electrodes is favored for most efficient operation, as low current density at the anode tends to increase the formation of chlorates.

The concentration of hypochlorite in the solution also affects the operation of the cell.[10] As a rule, the amount of reduction increases with the concentration of the hypochlorite, and finally a condition of equilibrium is reached where the hypochlorite is decomposed as fast as it is formed. The most economical concentration of hypochlorite to be employed varies with the type of cell under consideration. For the Haas-Oettel type of continuous cell, the concentration is about 4-5 grams of available chlorine per liter; in other types a concentration of 20-35 grams per liter may be used.

The nature of the salt used in the preparation of the electrolyte also has considerable influence on the operation of the cell. Crude salt will contain calcium, magnesium and iron compounds. These will be decomposed by the current and deposited on the electrodes, and this results in a number of complications. The resistance of the cell may be increased and the amount of reduction in the cell is also increased.

The concentration of the salt in the solution also influences the degree of dissociation of the sodium chloride in the electrolyte. A 10 percent solution of NaCl is dissociated to the extent of 60 percent into the ions Na and Cl respectively; a 5 percent solution is dissociated 69 percent, while a 1 percent solution is dissociated 81 per cent.

8. Cells for Electrolytic Hypochlorite Liquor.

One of the earliest types of cells adapted to the production of electrolytic hypochlorite liquors for bleaching purposes was that of Hermite. This cell used magnesium chloride as the electrolyte instead of common salt, for it was thought that magnesium hypochlorite was more rapid and efficient in its bleaching action. Owing to the relatively high cost of magnesium chloride, however, Hermite soon used a mixture of this salt with sodium chloride, as this was adopted for the further reason that the latter salt increases the conductivity of the solution.[11]

The following abstract from Hermite's patent describes the arrangement of the electrodes in his apparatus for the production of electrolytic bleaching liquors. The magnesium or calcium chloride, or other suitable solution, is submitted to the action of an electric current in a tank divided into two parts by a perforated partition; contained in the tank are the electrodes, preferably of zinc and platinum, and a screw propeller, which, by revolving, maintains a constant circulation

[10] Although rather concentrated solutions of common salt are employed as electrolytes, it is not possible to convert more than a small fraction of the sodium chloride into hypochlorite, for as the concentration of the latter rises, it is itself electrolyzed and reduced at the cathode.

[11] The following are his proportions: water, 1000 parts, sodium chloride, 50 parts, magnesium chloride, 5 parts. Hermite states that with his apparatus a motive power of ten horsepower can produce in 24 hours the equivalent of 100 kilos of chloride of lime at a cost of about $1.04 with use of hydraulic power, or about $2.00 with steam power

of the solution. The electrodes are so placed relatively to the openings in the partition that the solution in its circulation always comes in contact with these electrodes. The positive electrode is made up of thin plates of platinum cast into a suitable support at the top; by means of a mechanical device knives are kept constantly moving up and down over the surface of the zinc, to prevent any deposit accumulating thereon.

In an experimental study of the Hermite electrolytic method of bleaching, Cross and Bevan [12] have come to the opinion that the most advantageous solution to employ for the electrolyte is one containing 2.5 percent of anhydrous magnesium chloride, $MgCl_2$. Experiment demonstrated that the mean yield of available chlorine per ampère hour was 1.47 grams, whereas the equivalent calculated in accordance with the electrolytic law would be only 1.34 grams. This discrepancy is no doubt due to secondary reactions occurring around the electrodes. In order to express this result in terms of mechanical work (employing an electromotive force of 5 volts), we would have 1.47 grams of chlorine as equivalent to 5 watts. To produce 100 kilos. of available chlorine would therefore consume 344,000 watts; and taking 600 watts at the dynamo as representing one effective horse-power, it would require 570 h.p. to produce 100 kilos. of chlorine per hour. The efficiency of electrolytic chlorine appears to be greater than that of the available chlorine of bleaching powder; in fact, Cross and Bevan, from experiments on the actual bleaching of linen yarn, conclude that electrolytic chlorine has about twice the bleaching efficiency of the chlorine in bleaching powder.[13] Taking all these facts into consideration, the above chemists arrive at the conclusion that expressed in its equivalent per ton of bleaching powder, electrolytic chlorine would cost about $12.50.[14]

These results of Cross and Bevan, however, have been severely criticised by several chemists, and Hurter [15] carried out an extensive series of experiments to determine if any reliance could be placed on the work of Cross and Bevan. By very careful work Hurter has shown that the high current efficiency (100 percent of the theoretical) obtained by Cross and Bevan was entirely illusory and that the real current efficiency was much lower; being in fact only about 20 percent of the

[12] *Jour. Soc. Chem. Ind.*, 1887, p. 172.

[13] According to the experiments of Saget, Hermite's electrolytic bleaching liquor, containing only 0.3 gm. of available chlorine per liter gives a very pure white, whereas with bleaching powder, double this concentration is necessary to give the same effect. According to the experiments of Beadle (*Chem. News*, 1897, p. 74), the efficiency of the chlorine in the Hermite electrolytic bleaching liquor compared with that of the chlorine in ordinary bleaching powder is about 5 to 3; and furthermore, the Hermite solution bleaches in 30 minutes to the same degree as bleaching powder solutions of the same strength would do in 3 hours.

[14] For the cost of bleaching electrolytically, see *Faerber-Zeitung*, 1904, p. 69. It is said that 500 kilos. of goods can be bleached in the usual manner with 2000 liters of bleaching powder solution containing 2.5 to 2.7 gms. of available chlorine per liter By Schuckert's system and apparatus for electrolytic bleaching this amount of chlorine can be produced by the electrolysis of a 10 percent solution of sodium chloride, giving a liquor containing 20 gms. of available chlorine per liter This requires 29 kilos of salt, and the power necessary is 41 ampères at 110 volts for 8 to 9 hours, or 39.6 kilowatt hours; there would also be required 2 liters of sulfuric acid. Taking all this into consideration at the prices prevailing in Germany, (1912) it is claimed that the total cost compares favorably with that of 2000 liters of bleach solution of 1½ to 1¾ degrees Beaumé, or 42 kilos. of 32 percent bleaching powder, and 10 liters of sulfuric acid required for the same quantity of goods by the usual process.

[15] *Jour. Soc. Chem. Ind.*, 1887, p. 337.

theoretical. As to the higher bleaching efficiency of the chlorine (or chlorine compounds) in the electrolytic liquor, as claimed by Cross and Bevan, this has likewise been disputed. Hurter claimed that the incongruities existing in the experiments of different chemists on this subject are due to the fact that in the electrolysis of a solution of magnesium chloride, a considerable amount of magnesium chlorate and perchlorate are formed, both of which bodies are useless for purposes of bleaching. Cross and Bevan, however, have shown by carefully

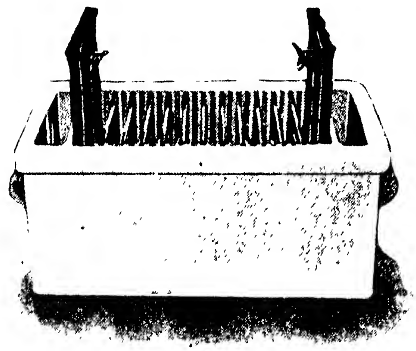


FIG. 180.—Small Electrolytic Cell Much Used in Laundries.

conducted experiments that in the Hermite bleaching cell no magnesium perchlorate whatever is formed. They establish the fact that an electrolyzed solution of magnesium chloride of an equal oxidizing strength as shown by the alkaline arsenious acid test, possesses a greater bleaching efficiency than one of calcium hypochlorite in the proportion of three to five; and the explanation given for this peculiar fact, which seems at variance with the usually accepted laws of electrolysis, is due to complicated secondary electrolytic reactions which give rise to a peroxidized compound of magnesium, and this latter body aids in the actual bleaching operation together with the chlorine.

9. Modern Types of Cells for Bleacheries.

There are two chief forms of electrolyzers at present in use for the preparation of bleach liquors; the one is known as the Kellner, and the other as the Oettel apparatus. In Kellner's apparatus the electrodes consist of platinum-iridium alloy, whereas with Oettel's apparatus the electrodes are carbon plates. The cells themselves consist of oblong tanks of vitrified porcelain which is not acted on by the chlorine or hypochlorite liquors. In this country there are a large number of cells of the Oettel type in use in laundries and small knit-goods mills, where they are worked with much satisfaction for the production of hypochlorite liquors on a small scale. Tests of this

apparatus have been made in large bleacheries, but it has always been found that the cost is prohibitive.

The Oettel electrolyzer is made in two forms; in the one a concentrated solution of hypochlorite is prepared containing about 14 grams of available chlorine per liter, while in the other a solution of hypochlorite containing about 4 grams of available chlorine per liter is produced in a continuous manner. This latter type is one now principally employed in small laundries and mills. The Oettel cell consists of a stoneware vat containing carbon electrodes with glass slips on the lower and upper edges. The cell proper is contained in a larger stoneware tank. This latter is filled with the salt solution to within 4 inches of the top. The cell is perforated at top and bottom in the

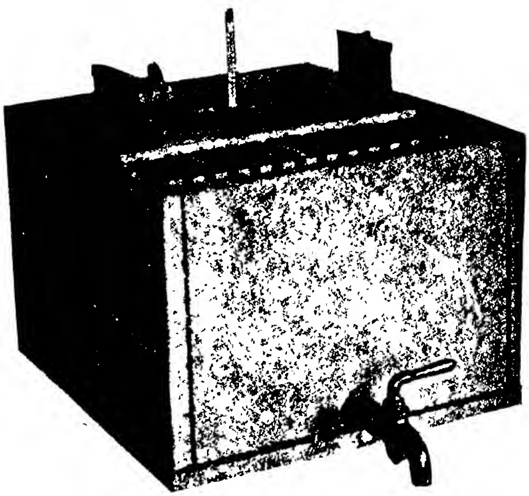


FIG. 181—Electrolyzer for Bleach Liquor.

sides which establishes a communication between each chamber formed by the electrodes and the outside solution. Circulation of the liquor through the cell is brought about by the liberated hydrogen lifting the liquor in the electrolyzer so that it flows out through the top holes into the outer tank. This causes fresh liquor to enter the electrolyzer through the bottom holes. In the older form where a concentrated liquor was produced the temperature of the liquor was kept down to 95° Fahr by cooling in the outer tank with a coil of pipe with cold water circulation. In this cell a 15 percent salt solution is used, with a continuous current of 110 volts and 75 to 80 ampères. In 10 hours running this will produce 750 gallons of hypochlorite liquor of 14 grams of available chlorine per liter. The power consumed is 88 kilowatt hours for 23 lbs. of available chlorine, or 3.83 kilowatt hours per lb. of chlorine. There is also a consumption of 12 lbs. of salt per lb. of chlorine. The cost of the chlorine therefore depends on the cost

of the electrical power and the salt. To this must also be added the depreciation of the electrodes; it is claimed that a set of electrodes will last about 12 months.

In the continuous type of Oettel apparatus the cell is smaller and the cooling coil is dispensed with as the cool brine solution is slowly running into the electrolyzer while the hypochlorite liquor (containing about 4 grams of available chlorine per liter) is continually flowing out. This aids the circulation of the liquor through the cell and also keeps it cooled to about 95° Fahr. This cell also runs with 110 volt direct current at about 40 ampères. Observation by the author of an installation of these cells in actual working practice gave the following data:

No. of cells used	4
Voltage of current	110
Current strength ampères	160
Gallons of hypochlorite liquor	400
Strength of liquor in grams per liter	3.55
Time of electrolyzing in hours	25
Salt used in lbs	200

The power used therefore was:

$$0.160 \times 110 \times 25 = 44 \text{ KWH}$$

The quantity of chlorine produced was 11.6 lbs. The cost of electrical power was 2½ cts. per KWH; the cost of salt was $4.00 per ton (of good quality). Therefore, the following cost figures result:

		¢
Power	44 KWH @ 2½¢ =	110
Salt	200 lbs @ 0.2 =	40
	11.6 lbs. chlorine =	156
	or 1 lb chlorine =	13.4¢

In this particular instance, the deterioration of cells was $60.00 per year for production of about 7000 lbs. of chlorine per year. Hence, an item for depreciation of 0.85 ct. must be added to the above cost figure, making the total cost per lb. of chlorine as about 14.25 cts. This probably represents a fair estimate for this process of producing electrolytic bleach liquor in small installations.

10. Factors in Operation of Electrolytic Cells.

In the consideration of forms of apparatus for the electrolytic preparation of bleach liquors the following factors should be compared:

(a) *Amount of salt required per pound of "active" chlorine produced.* It must be remembered that the greater part of the salt consumed does not take any part in the chemical decomposition brought about by the electrolysis, and only serves the purpose of acting as a conductor for the current, though it also aids in the efficiency of the cell by preventing improper reactions at the anode. The higher the salt concentration the less will be the power required per pound of

electrolytic chlorine. For a bleach liquor free from any excess of salt there would be required theoretically 0.82 lb. of salt per lb. of "active" chlorine, but in the best apparatus there will be required at least 3 lbs. of salt per lb. of chlorine, and in practice with different forms of apparatus the salt consumption per lb. of "active" chlorine varies from 3 lbs. to 15 lbs.[16]

(b) *Power consumption per pound of "active" chlorine.* This varies considerably with different types of apparatus and the form of their construction, there being indeterminate losses through secondary reactions. It is also dependent on the salt concentration of the electrolyte. The theoretical figure for power consumption is never reached in practice, this figure being 0.57 kilowatt hours per pound of "active" chlorine. As the higher the salt concentration the lower is the power consumption, it will be a matter of adjusting these two factors with a consideration of their relative costs in order to obtain the most economical conditions for operation. The following table worked out by W. Eb for the Siemens & Halske system of electrolyzer shows some interesting comparisons with regard to power consumption for different conditions of operation:

Salt used in 100 liters solution	10 kilos.			12 kilos.			15 kilos.		
Required for 1 kilo. of active chlorine	kilo-watt hours	horse power hours	kilos of salt	kilo-watt hours	horse power hours	kilos of salt	kilo-watt hours	horse power hours	kilos of salt
For a bleach liquor concentration of:									
15 gms. active chlorine per liter	5.65	8 5	6 67	5 46	8 2	8 00	5 29	7 9	10 00
20 gms. do.	6 13	9 2	5 00	5 83	8 7	6 00	5 56	8 3	7 50
25 gms do	6 72	10 1	4.00	6 27	9 4	4 80	5 88	8 8	6 00
30 gms. do.	7 79	11.7	3 33	6 98	10 5	4.00	6 38	9 6	5 00
35 gms. do	10 07	15.1	2 86	8.20	12 3	3.43	7.14	10 7	4 28

The kilowatt hour was assumed to be equal to 1.5 horsepower hour, and the power consumption was on a basis of a potential of 6 volts.

(c) *Yield of chlorine in a definite time.* Depending on requirements in this respect the size of the apparatus is varied. Also consideration must be had as to whether a continuous production of dilute bleach liquor is required simultaneous with the bleaching operations, or if it is desired to produce a strong stock bleach liquor which may be suitably stored and diluted when required for use. In this connection, however, it must be borne in mind that electrolytic bleach liquors are not very stable as prepared, and if such liquors are prepared in concentrated form and stored, a small amount of caustic soda should be added to the liquor to give it greater stability.

(d) *Concentration of the electrolytic bleach liquor.* A high chlorine strength is generally desirable, so that the bleach liquor may be suitably

[16] In some countries, as in Germany, where edible salt is taxed, it is customary to denature salt for technical use by the addition of petroleum, soda ash, soap, methyl violet, bleaching powder, etc. The most usual product employed for electrolysis is rock-salt denatured with ¼ percent of petroleum.

diluted as occasion demands. Also it is to be noted that a low content of bleaching chlorine necessitates a high salt concentration, whereas with a high chlorine content the relative salt concentration for the same strength of actual bleach liquor is much lower. The chlorine concentration, however, reaches a practical maximum, depending on power-consumption, stability of liquor and extent of secondary reactions. When the chlorine concentration becomes too high, further electrolysis produces decomposition resulting in the formation of chlorates or the liberation of oxygen, and the efficiency of the cell rapidly runs down. In this connection Nussbaum and Ebert give the following tabulated results from the operations of a Siemens & Halske electrolyzer:

Duration of electrolysis in hours	Ampères	Volts	Grams active chlorine per liter	Kilos. of active chlorine produced	Kilos. per hour	Efficiency percent	1 kilo. active chlorine requires		1 kilo of chlorine costs (pfg.)
							Kilowatt hours	Kilos salt	
0	120	110	(0.6)	....	(3.7)	(100)	(4.2)	...	...
1	120	120	10.0	3.01	3.01	94.9	4.6	18.4	46.0
2	118	118	18.1	5.60	2.80	88.6	5.0	9.9	29.7
3	118	118	25.3	7.90	2.63	83.7	5.3	7.0	24.6
4	117	119	31.6	9.92	2.48	79.1	5.6	5.6	22.4
5	116	120	37.0	11.65	2.33	74.5	6.0	4.7	21.5
6	118	120	41.6	13.12	2.19	70.1	6.4	4.2	21.2
7	115	119	45.3	14.30	2.04	65.6	6.8	3.9	21.4
8	117	120	48.0	15.17	1.90	61.0	7.4	3.6	22.0
9	116	120	49.8	15.74	1.75	56.3	8.0	3.5	23.0

The apparatus had been in previous use which accounts for the small quantity of chlorine in the fresh liquor. The theoretical amount of chlorine produced per hour was 3.12 kilos., and the ratio of the total quantity of chlorine produced to that required by theory is 15.74: 28.08, or a current efficiency of 56 percent. In most cases in practice and depending on the type of apparatus used the best chlorine concentration of the bleach liquor is 5 to 30 gms. per liter.

(e) *Cost of installation of the electrolyzer and the subsidiary equipment.* Some forms of cells require platinum electrodes which at the present time are exceedingly costly and almost prohibitive in comparison with carbon electrodes which are used in other types of cells. On this account, the latter form of cell is almost entirely used at the present time. The cost of upkeep and depreciation must also be considered. It is highly desirable that the apparatus be "fool-proof" and its various parts must be capable of resisting the chemical action of chlorine and salt solutions, so special materials have frequently to be used in the construction, and these must be sturdy and durable.

(f) *Stability of the electrolytic bleach liquor.* As already pointed out the bleach solution coming from the cell is not very stable in character. The stability, however, varies with the chlorine content, the salt concentration, the temperature and the alkalinity of the solution. As ordinarily prepared, electrolytic bleach liquors will lose from 30 to 50 percent of their "active" chlorine on standing overnight. The content of free hypochlorous acid in the liquor materially affects its

stability; on this account electrolytic bleach liquors are generally less stable in character than those prepared from liquid chlorine dissolved in alkaline solutions as in the latter case there is usually sufficient free alkali always present to avoid the formation of free hypochlorous acid. In case electrolytic bleach liquors are so kept (as stock solutions) for any length of time it will be necessary to add to them some caustic soda in order to maintain the liquid in a definite condition of alkalinity. The effect of the alkali on the keeping qualities of bleach liquors is shown in the following table of tests:

500 c.c. Electrolytic Bleach Liquor	Acidity Gms HOCl per liter		after:				
			Fresh	2 hrs.	1 day	3 days	8 days
No added alkali.	1 869	acid	19.8	11.9	3.18	2.38	1.12
2.5 c.c. caustic soda (1.10)	1 326	acid	19.6	14.8	3.95	1.98	1 02
5.0 " " " " .	0.775	acid	19.5	17.4	8 5	3 28	0 82
10 0 " " " " .	0 392	alkaline	19.3	19.1	19.0	18.4	17 4
15.0 " " " " .	1 695	alkaline	19.0	18.8	18.7	18.3	18.1
20.0 " " " " .	2.796	alkaline	18 9	18.7	18 6	18 1	17 9

Probably the most common form of electrolyzer in use in this country in the small textile bleacheries and laundries is that patterned after the Haas & Oettel type. The bleach liquor is prepared continuously, the fresh salt solution running into the cell and the corresponding amount of bleach liquor running out. The liquor so prepared seldom has a chlorine content of over 4 gms. per liter, and of course the salt concentration is rather high. When operating under proper conditions the liquor is practically neutral and its stability is low. It is generally the practice in this case to use the liquor for bleaching as fast as it is formed and then it is not necessary to add any caustic soda to it. If it becomes necessary, however, to hold the liquor over for any length of time a small addition of caustic soda solution should be made, sufficient at least to give it a pronounced alkaline reaction with litmus. The use of excessive alkali, however, is to be avoided, as this slows down the bleaching activity of the solution.

A form of electrolytic bleach cell popular in Germany is the Schuckert cell (Siemens & Halske). This cell, however, requires a platinum-iridium anode and graphite cathode. It gives a liquor of high chlorine content of 15 to 30 gms. per liter, and it is possible to produce a liquor having as high as 50 gms. of active chlorine per liter. The Schuckert cell, however, has a rather high efficiency, the power consumption per kilo of active chlorine being 5.5 to 7.5 kilowatt hours, and the salt consumption being 4.5 to 10 kilos.

Higgins[17] gives an interesting comparison of electrolytic bleach liquors with those of chloride of lime and sodium hypochlorite. It was found that the electro-chemic was always alkaline, as in fact must be the case, for there is always a slight loss of chlorine in the cell due to the lack of perfect circulation and the consequent complete combination

[17] *Jour. Soc. Chem. Ind.*, 1911, p 185.

of all the chlorine with the caustic soda formed. The better the circulation the less the alkalinity and the more active the electro-chemic. The following solutions were prepared: (1) Electro-chemic by electrolyzing a solution of 220 lbs. of salt in 186 gallons of water for 8 hours at a temperature of 20° C. with a current of 50 amps. and 110 volts; (2) bleaching powder solution carefully prepared with a gravity of 1.08; (3) from this was also made the sodium hypochlorite solution by adding soda ash solution to complete precipitation. As to the stability of these three liquors when exposed to the air, it was found that they were practically identical over a series of tests, ranging from 3 hours to 120 hours. It has often been claimed that agitation will decompose the electro-chemic, but on severely agitating all three liquors in flasks for several hours there was no evidence of appreciable decomposition in any of them. To test the bleaching effect brown linen cloth was used and the liquors were titrated for content of active chlorine from time to time; the results showed that there was practically no difference between the rates of bleaching of the three liquors, the bleaching powder solution bleaching as rapidly as the electro-chemic. After bleaching the strength of the cloth was tested and there was no appreciable difference between the three. During bleaching the liquors became milky in all cases to about the same degree, and acid was used to clear the cloth in all cases, and after bleaching the three samples of cloth were of approximately the same color and could not be distinguished from each other. The electro-chemic, as well as the other chlorine solutions, were found to be difficult to wash out from the cloth. On testing the stability of the bleach liquors when acidified there was practically no difference to be observed in the three cases. As to the rate of bleaching of the acidified liquors it was found that the bleaching effect was similar, and that the sodium hypochlorite bleached as rapidly as the electro-chemic, the bleaching powder solution being only a little slower in action. The addition of a relatively large amount of common salt (120 grams per liter and equal to that present in the electro-chemic) to the sodium hypochlorite solution only slightly decreases its stability and increases its bleaching effect; the addition of caustic soda increases the stability and decreases the rate of bleaching. All three of the original chemic solutions had a greenish color which was about the same in all cases; the addition of acid intensified this color and made the stability less, while caustic soda took most of the color away and increased the stability. In comparing the properties and efficiency of the different bleaching liquors it is important that they all possess the same degree of alkalinity, otherwise the comparison is worthless. Sodium hypochlorite in practice is nearly always in a rather highly alkaline state, and dilute bleaching powder liquors are more alkaline (contain more dissolved lime) than concentrated liquors.

11. Effect of Hypochlorite Bleaching on Cotton.

In the bleaching of cotton, the fiber is subjected to the action of strong chemicals, therefore, it is interesting to know if the strength of the fiber is seriously affected by the various bleaching operations.

Scheurer has investigated this matter, and has found that when cotton is heated with water under pressure to 150°C. no tendering effect is to be observed, even though the action is continued for 8 hours. At temperatures above 160°C., however, the tendering action of water becomes well marked and considerable. Heated in contact with the air for 1 hour at 170°C., the cotton did not appear to become weakened; this fact is interesting in view of the operation of singeing which cotton cloth generally undergoes before bleaching. Haebler gives the following tests on the strength of cotton cloth after the various bleaching operations:

Stage of bleaching	Breaking strain in kilos.
Unsized cloth	4.656
Singed	5.206
Boiled in lime and washed	4.694
Soured with hydrochloric acid and washed.	4.664
Boiled in soda and washed	4.799
Treated with chlorine and washed	5.204
Soured with sulfuric acid and washed	5.345
Dressed	6.423

Cross and Bevan from a series of experiments on the bleaching of vegetable fibers have arrived at the following conclusions:

(1) Bleaching by means of hypochlorites is attended with the chlorination of the fiber constituents. (2) The chlorination is much less where magnesium hypochlorite is used, and still less where solutions prepared by the electrolysis of magnesium chloride are employed. (3) The evidences of chlorination are that a portion of the chlorine in the bleaching solution is not converted into the chloride, and organic chlorides are found to be present in the washed material. (4) The cause of chlorination probably lies in the presence of ketonic oxygen in the non-cellulose constituents of the fiber.

Chapter XIX.

The Bleaching of Cotton *(Cont.)*.

1. Bleaching with Permanganate.

As already mentioned under the bleaching of wool, potassium permanganate is a powerful oxidizing and bleaching agent, and it may be used for bleaching cotton in a manner similar to that employed for wool. The cotton is steeped in a cold dilute bath of potassium permanganate containing a small quantity of sulfuric acid. The permanganate gives up its oxygen and becomes thereby reduced to a hydrated oxide of manganese which is precipitated on the fiber as a dark brown deposit. To remove this brown compound of manganese it is necessary to rinse the cotton in water and then pass into a fresh bath consisting of a dilute solution of sodium bisulfite. A bath of oxalic acid may also be employed for the same purpose.

Alkaline solutions of permanganate should not be used with cotton, as the fiber will be rapidly disintegrated through the formation of oxycellulose; on this account slightly acid solutions are employed.

To bleach 100 lbs. of cotton prepare a bath containing 9 oz. of potassium permanganate and 7 oz. of sulfuric acid. Steep the material in this bath for 15 minutes at about 60° to 70° Fahr. Then squeeze and rinse in fresh water, and pass into a second bath containing 11 oz. of sodium bisulfite liquor of 38° Bé.

According to Manzoni, cotton may be very efficiently bleached with potassium permanganate in the following manner: The well boiled-out cotton is steeped for several hours in a solution of sulfuric acid at 6° to 8° Tw., during which small portions of potassium permanganate are added from time to time. The cotton is said not to turn brown, and a subsequent treatment with sodium bisulfite is hence necessary, while ½ percent of potassium permanganate is said to effect a good bleach.[1]

[1] Manzoni's experiments were as follows: Solutions of ½, 1, 1½ and 2 parts of potassium permanganate per 100 parts of cotton were used, the quantity of water in the bath being 30 parts to 1 of cotton; the cotton yarn employed was first boiled out in a caustic soda solution of 4 gms. per liter under 2 atmos. pressure, then well washed and steeped for 5 hours in the permanganate bath containing sulfuric acid to a strength of 5° Bé. The permanganate was added in several different proportions, the solution was well stirred and the temperature raised from 15° to 20° C. Similar experiments were also made with neutral and alkaline solutions of potassium permanganate, and the conclusions were as follows: In neutral solutions the reduction of the salt takes place regularly but slowly; in alkaline solutions the reduction probably takes place in two stages; in the first, the color changes rapidly from violet to green, and when the cotton is entered a partial precipitation of manganese hydrate occurs on the fiber; in the second the green manganate loses its color very slowly, the manganate remaining in solution being precipitated on the fiber very slowly. In the acid solution, the reduction takes place much more regularly and in less time than under the other two conditions. At the end of each series of experiments, when the permanganate was reduced, the yarn in all three cases was of a brown color, which was darker, however, than that treated in the acid bath. The difference in the strength of the fiber was quite perceptible. The yarn which was treated in the acid or neutral bath was not tendered at all, but that which was treated in the alkaline bath was tendered throughout, especially where the 2 percent solution of permanganate was used.

The use of the acid bath prevents the formation of the oxide of manganese in the fiber, as in the reaction between the permanganate and the sulfuric acid, manganese sulfate and oxygen are formed as follows:

$$K_2Mn_2O_8 + 3\ H_2SO_4 = 2\ MnSO_4 + K_2SO_4 + 3\ H_2O + 5\ O.$$

According to a process recently patented in England, potassium permanganate may be employed in conjunction with bleaching powder

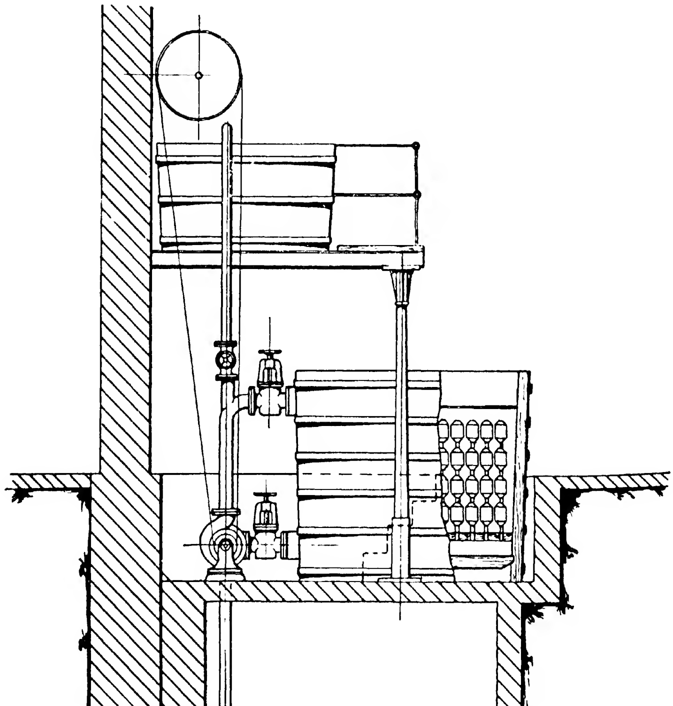


Fig. 182.—Bleaching Apparatus for Cotton Roving.

for purposes of bleaching cotton fabrics in the following manner: The cloth to be bleached is packed in a bath containing 8 gallons of bleaching power solution of 10° Tw., and 2 lbs. of potassium permanganate. The goods remain in this bath for 2 to 3 hours, and are then washed in water, after which they are then placed in a second bath containing 7 lbs. of sodium bisulfite and 3/4 pint of sulfuric acid. They are left for 1 1/2 hours in this bath and then well washed again. These opera-

tions are repeated by giving a third bath containing 3½ gallons of bleaching powder solution at 10° Tw. and 6 oz. of potassium permanganate and a fourth bath of 2½ lbs. of sodium bisulfite and ½ pint of sulfuric acid.

A rapid process for the bleaching of cotton goods by the permanganate process is given as follows by Delebecque.[2] The material is successively worked in the following baths: (1) 2 kilos. of caustic soda and 2 kilos. of soda ash to 1000 liters of water; time of immersion ½ to 2 hours; (2) a 0.5 percent solution of sulfuric acid for 10 minutes; (3) a 3 percent solution of potassium permanganate for 3 to 5 minutes; (4) solution of 3 kilos. of barium peroxide and 10 kilos. of hydrochloric acid to 100 liters of water for 15 to 20 minutes; (5) a solution of 200 liters of hydrogen peroxide (12 vols.), 4 kilos. of borax, and 10 kilos. of white soap to 800 liters of water for ½ to 1½ hours. Baths (1) and (5) are used at a maximum temperature of 80° C., and operations (3) and (4) may be repeated several times if necessary. It would seem that such a process as this would be very costly and could be applied only to small articles of value where close personal attention to the operations could be given.

Müller has proposed a novel method of bleaching cotton with permanganate in connection with air, the permanganate supposedly acting as a catalytic agent. In carrying out the process 60 lbs. of cotton cloth are treated in a closed vat or kier with 1000 lbs of 1 percent solution of caustic soda containing 1 oz. of potassium permanganate. In order to avoid the formation of oxycellulose the cloth should be packed in such a manner as to be completely submerged beneath the liquor. The cloth is then boiled for 2 hours under a pressure of 2 atmospheres, and then a current of air is forced in under a pressure of 3 atmospheres.[3] When the liquor has acquired a clear yellow color, which usually requires about 12 hours, the process is completed, and the cloth is well washed with water and then treated with a ½ percent solution of sodium bisulfite for the purpose of removing the hydrate of manganese. It is finally soured, washed and dried. By this means it is claimed that boiling-out and bleaching can be executed in one operation.

The potassium permanganate method of bleaching is of but little importance for cotton on account of its high cost as compared with bleaching powder. It has some use, however, in the bleaching of linen and jute, though even in these cases it is usually employed in connection with chloride of lime. As compared with chloride of lime, the permanganate bleach has a greater effect on the strength of the fiber and is more liable to cause local oxidation. On the other hand, the bleaching effect is much more rapid, the oxidation taking place in the course of a few minutes. Heating the permanganate solution also rapidly accelerates the bleaching action.

The bleaching (or oxidizing) effect of a permanganate solution

[2] *Fr. Pat.* 412,010.

[3] It has also been suggested to add hydrogen peroxide or sodium peroxide to the liquor instead of blowing air in under pressure in order to furnish the necessary oxygen for the bleaching.

differs considerably, depending on whether the solution is acid or alkaline (neutral); in the former case 5 atoms of oxygen are available, whereas in the latter case only 3 atoms of oxygen are set free:

$$2\ KMnO_4 + 3\ H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + 5\ O.$$
$$2\ KMnO_4 + 3\ H_2O = 2\ KOH + 2\ MnO_2.H_2O + 3\ O.$$

If acid is not present, hydrated manganese dioxide is precipitated and the solution becomes alkaline owing to the formation of potassium hydrate. If the precipitation of the brown manganese compound is to be avoided the solution has to be made rather strongly acid, requiring a sulfuric acid concentration of about 70° Tw., which is rather dangerous to the fiber.

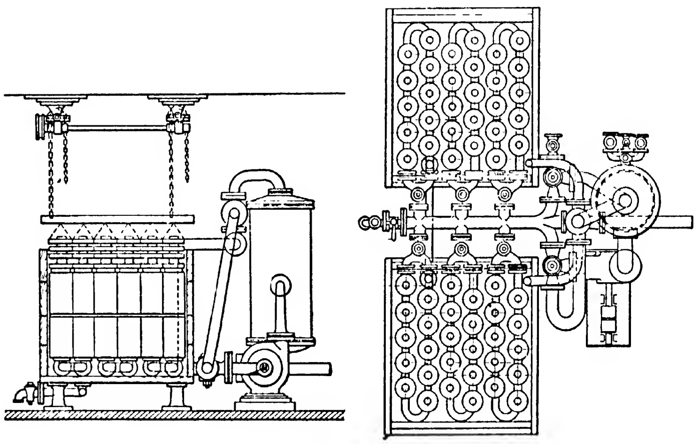


FIG. 183.—Card Sliver Bleaching Machine

The rapidity of the permanganate bleach in the case of vegetable fibers does not allow of a well penetrated bleach with the consequence that the inner parts of the fiber are not properly bleached, and, though the surface may at first appear quite white, this superficial purity is liable to be lost after a time. This is especially true if all trace of the manganese compounds are not thoroughly washed out.

2. Bleaching with Peroxides.

The use of the various peroxide bleaching salts is accompanied by less danger to the material than is the use of the hypochlorite compounds; this being especially true when used on a small scale and by persons who are not expert in the particular technique of bleaching. The peroxide compounds may also be used for the bleaching of all classes of fibers, and, in fact, of all kinds of materials whether textiles

or not, whereas hypochlorites are only applicable to vegetable fibers. On the other hand, in the latter case, the peroxide agents are more expensive than hypochlorites, and it is more difficult to obtain as high a degree of bleaching. The peroxide bleaching agents, however, may be used in connection with other cleaning agents such as soap powders and alkaline detergent preparations, being mixed directly with these compounds to form a single cleaning and bleaching product, which is often of great convenience to the small scale user who may not be technically equipped to carry out involved bleaching processes. Such preparations are especially adapted for small laundries and household use.

Use of Hydrogen Peroxide.—This bleaching agent may be employed for cotton in the same manner as for wool. Of course, it acts merely as a decolorizing agent, and simply replaces the treatment with chloride of lime; the cotton must be boiled-out in the same manner as for the ordinary method of bleaching. The following procedure for bleaching cotton with hydrogen peroxide is given by Koechlin: For 50 kilos. of cloth use a bath containing

Water	100 liters
Caustic soda	10 kilos.
Soap	30 kilos.
Calcined magnesia	5 kilos.
Hydrogen peroxide (12 vol.)	50 liters

The goods are to be boiled in this solution for 6 hours; wash, and then pass through sulfuric acid of 3° Tw., and wash again. The magnesia is added to the bath in order to prevent the too rapid decomposition of the hydrogen peroxide, as otherwise the oxygen would be liberated so fast that it would have no chance to do any bleaching. The magnesium oxide, no doubt, forms a peroxide which decomposes but slowly at a boiling temperature. A magnesium soap is also formed through the interaction of the soap in the bath and the magnesia, but this is rather easily removed in the washing and treatment with acid.

The method of Siebold and Schwartz for cotton bleaching is as follows: The goods are boiled-out in the usual manner, then saturated with a dilute solution of hydrogen peroxide and hung in a special chamber in which they are subjected to the action of warm vapors of ammonia. At the end of an hour the bleaching process may be considered as finished.

Use of Sodium Peroxide.—Sodium peroxide is a cheaper agent to employ for bleaching than hydrogen peroxide, and its action in bleaching is exactly the same, because the active bleaching agent in each case is hydrogen peroxide. The bath of sodium peroxide for use with cotton goods is prepared in the same manner as for wool and the operations are carried out in just the same way (see page 137). As a rule, for the majority of cotton goods, the peroxide bleach is too costly to have any practical application. It is sometimes used for delicate and costly materials where it is feared that the treatment with chloride of lime, acids, etc., would injure the fabric; it is also used at times for the bleaching

of silk and cotton mixed goods. The following table is given as the best conditions for bleaching the different fibers with sodium peroxide:[4]

Fiber	Percent of sodium peroxide in bath	Temp. °C	Time in hours	Percent of sodium peroxide on weight of goods
Cotton	1	30—40	1—3	1
Linen	1	40—50	10—11	1
Wool	2—3	50	4—5	2—3
Silk	4—6	80	4—8	3—5
Straw	1	30—40	2—4	1—2

In the bleaching of cotton with sodium peroxide the bath should show a strength of ½ to 1 percent of hydrogen peroxide, and it is found that the required consumption of sodium peroxide is about ½ to 1 percent of the weight of the goods. The time necessary for bleaching varies from ½ to 10 hours, being dependent on the character of the goods bleached, the alkalinity of the bath and its temperature, which may vary from 90° to 180° F., according to circumstances.

Though cotton itself is seldom bleached with sodium peroxide, the method is considerably used for the bleaching of mixed goods, such as silk-cotton and wool-cotton fabrics. In dealing with such mixtures, it must be borne in mind that, though cotton will stand a boiling peroxide bath, wool must not be treated at temperature above 130° to 140° F. The following formula is said to give good results in the bleaching of wool-cotton fabrics:

Water	100 gallons
Magnesium sulfate	15 to 30 lbs.
Sulfuric acid	1¼ to 3½ lbs
Sodium peroxide	5 to 10 lbs.

The goods are well scoured and steeped in the above bath at 140° F. for 4 to 8 hours. With silk-cotton fabrics, the bath is finally raised to the boil.

An excellent qualitative test for residual hydrogen peroxide in old bleaching solutions is the use of a sulfuric acid solution of titanium sulfate; this gives a yellow color with hydrogen peroxide which is quite characteristic.

In order to determine accurately the residual hydrogen peroxide left in old bleaching baths, titration with potassium permanganate cannot be employed, as the organic impurities accumulating in the bath from the fiber materially affect the result. Kind[5] calls attention to a much better method; the solution to be analyzed is first strongly acidified

[4] According to the manufacturers, the cost of bleaching various articles with peroxide of sodium is as follows (1913):

Wool, raw and piece goods	$1 00	to	$1 75
Mixed, Union, and Knit goods	1 00	to	1 50
Mixed wool and silk, cotton and silk	1 50	to	2 50
Silk, skein and piece	2 00	to	3 00
Cotton	60	to	75
Tussah silk	4 00	to	7 00
Jute, hemp, flax	50	to	1 00

These figures are supposed to cover the cost of the chemicals per 100 lbs. of goods bleached

[5] *Bleichen der Pflanzenfasern*, p. 167.

with sulfuric acid and there is then added an excess of potassium iodide. The hydrogen peroxide present sets free iodine which is then titrated with 1/10 normal sodium thiosulfate solution. It is necessary to have the solution first acidified, as potassium iodide acting on hydrogen peroxide in alkaline solution does not set free iodine, but liberates oxygen.

Ozone itself has been tried as a bleaching agent, but it has proved to be too expensive for general use. Ozone is produced by high tension

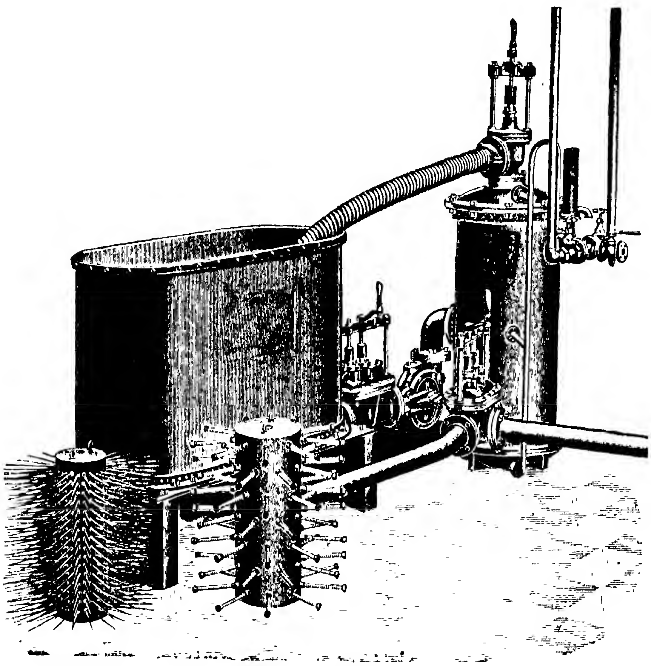


FIG. 184.—Open Bleaching Machine for Cops and Tubs.

electrical discharges in air, and is simply oxygen in a condensed molecular state. The molecule of oxygen in its ordinary condition is considered as consisting of two atoms of oxygen, O_2, whereas ozone consists of oxygen, O_3. The bleaching activity of ozone is very high and if it were possible to produce it cheaply enough it would make a very acceptable bleaching agent.

Schreiner has proposed a method of using finely divided turpentine to ozonize the oxygen of the atmosphere. Turpentine is also an excellent solvent for ozone. The method is carried out by dissolving 125 parts of resin in 250 parts of turpentine, and then adding a mixture of 22 parts of caustic potash, 40 parts of water and 90 parts of hydrogen

peroxide. This gives a clear liquor, which is exposed for 2 to 3 days to bright sunlight and then kept for a week in the dark. This causes the formation of a stable solution which is given the name of *ozonine*. An emulsion of 1 part of ozonine in 1000 parts of water is said to be of sufficient strength for the preparation of bleaching baths for the treatment of cotton.

A rather unusual method of bleaching by utilizing the oxygen of the air is given by Muller[6] as follows: 60 kilos. of cotton and 1000 liters of a 1 percent solution of soda ash containing also 20 grams of manganese sulfate are put into a closed kier, taking care that the cotton is completely immersed. The lye is heated for 2 hours under 2 atmos. pressure, air being excluded. A current of air at a pressure 1 atmos.

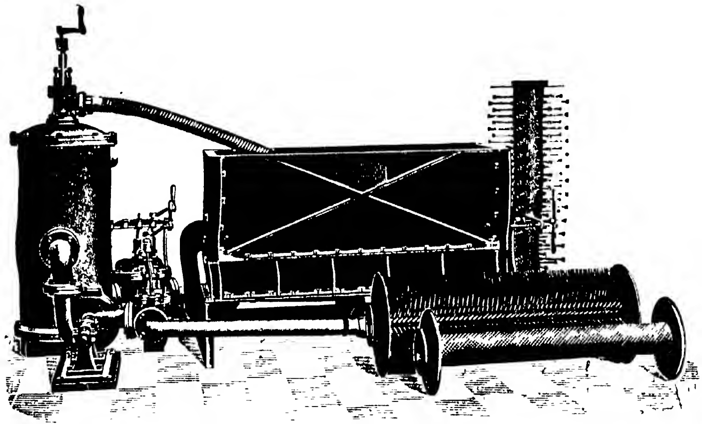


FIG. 185.—Open Horizontal Bleaching Machine for Beamed Warps.

greater than the steam pressure is then directed on to the surface of the lye until the bleaching operation is complete. The lye is then run off and the cotton is washed, treated for a brief time with a 0.5 percent solution of sodium bisulfite to remove the precipitated manganese compound, washed again and finally dried.

The so-called "air bleach" for loose cotton is given by Müller as follows:[7] From 2500 to 3000 pounds of loose cotton are placed in an upright kier (about 9 feet high and 9 feet in diameter), together with about 3700 gallons of a 1 percent solution of caustic soda, and boiled under a pressure of 2 to 2½ atmospheres with constant circulation and free from air for 12 to 15 hours. Then by means of a compressor air under 4 atmospheres pressure is forced into the circulating liquid and the boiling continued for 2 hours longer. By means of a suitably regulated valve the air is evacuated as it is used up. It is claimed that the cotton is bleached a satisfactory white, especially if soured afterwards

[6] *Fr. Pat.* 414,821.
[7] *Ger. Pats.* 240,037 and 242,296.

with a ½ percent solution of hydrochloric acid. Modifications of the process are suggested in the use of metallic catalyzers such as manganese carbonate (0.01 percent) or cobalt oxide (0.5 percent) to the alkaline lye and boiling in the presence of compressed air under 2 atmospheres pressure for 12 hours. It would seem that in this process it is necessary to suspend the material in the lye and not to have the air come directly in contact with the goods, but only as a solution in the lye, otherwise oxycellulose will be formed and the fiber weakened.

In the preparation of peroxide bleaching solutions for cotton goods (or linen) there have been numerous methods suggested in the technical and patent literature.

Jacobsen [8] gives the following: The goods are first given a cold sour with sulfuric acid at 2° Tw., rinsed and boiled for 6 hours in a pressure kier with a liquor consisting of 350 gallons of water, 48 gallons of hydrogen peroxide (12 vol.), 200 pounds of calcined magnesia and 50 pounds of soap.

Königsworter and Ebell give the following method: The goods are first boiled-out as usual with soda ash and caustic soda lye; the bleach bath is prepared with 10 gallons of hydrogen peroxide (12 vol.) diluted with 5 to 6 times the quantity of water and 1 quart of ammonia water. Steep the goods in this solution for 8 to 10 hours at a temperature of 80° to 90° F.

In some methods (particularly for use on low-grade carded cotton containing a large quantity of motes and impurities) it is recommended to give the goods a preliminary bleaching with sodium hypochlorite, and after thorough washing to then bleach with the peroxide bath. In such cases it must be remembered that hydrogen peroxide acts as an antichlor with hypochlorites; that is to say, the peroxide and hypochlorite mutually neutralize one another. Therefore, care should be taken not to carry over residual hypochlorite liquor in the goods to the peroxide bath, as in such a case the peroxide would simply be decomposed without exercising any bleaching effect on the goods being treated.

Attempts have been made with more or less success to use the peroxide bleach on cotton in connection with a boiling-out operation. Gagedois [9] recommends the following: For 100 pounds goods prepare a bath with 1 to 3 pounds sodium peroxide, 1 to 4 pounds ordinary white soap and 2 to 8 pounds soda ash. Treat the material in this bath for 4 to 6 hours, starting at 120° F. and gradually raise to the boil. While this method may furnish a satisfactory white color on a fine quality of clean cotton goods prepared from combed yarns, it is doubtful if very gratifying results will be obtained on the lower grades of cotton material when a considerable amount of highly resistant impurities are to be met with. This process has received more encouragement in linen bleaching and has been operated with considerable success in a large French bleachery for fine linen goods, and is claimed to be a satisfactory substitute for grass bleaching.

[8] *Ger. Pat.* 21,081.
[9] *Ger. Pat.* 130,437.

3. Bleaching Cotton with Perborates.

Solutions of sodium perborate may be employed for the bleaching of cotton goods in a somewhat similar manner to sodium peroxide. As the cost of bleaching in this manner, however, is relatively high, sodium perborate would not, as a rule, be employed except for the bleaching of very high grade cotton materials, such as laces, etc.

Bleaching solutions of sodium perborate are rather sensitive to the catalytic action of various metals. In order to inhibit such reactions Sarason [10] recommends the addition of sodium pyrophosphate; Byk [11] uses sodium bisulfate and in *Ger. Pat.* 250,262 the use of borax is mentioned.

In the use of sodium perborate the active bleaching agent is hydrogen peroxide, as the following reaction takes place when this salt is dissolved in water:

$$\underset{\text{Sodium Perborate}}{4\,NaBO_3} + \underset{\text{Water}}{5\,H_2O} = \underset{\text{Hydrogen Peroxide}}{4\,H_2O_2} + \underset{\text{Borax}}{Na_2B_4O_7} + \underset{\text{Caustic Soda}}{2\,NaOH}$$

It will be seen, therefore, that the resulting solution is alkaline, containing both borax and caustic soda. The sodium perborate solution, however, is less alkaline in character than the corresponding solution of sodium peroxide.[12]

Notwithstanding some attractive features in the use of perborates for bleaching, particularly their comparative stability even in boiling solutions, their use has not met with any great degree of favor, perhaps chiefly owing to the higher cost of these chemicals, and the fact that the results obtained are either not as good or in nowise better than those obtained in the older and well established forms of bleaching.

A process for bleaching yarn and piece-goods on a large scale by means of perborate (Perborin) has been patented by the Chemische Fabrik Grünau.[13] For yarn the process is as follows: 2000 lb. of cotton yarn is soaked in boiling water for about half an hour, rinsed, centrifuged, and packed in a boiler, provided with a circulating pump. The goods are then heated in the bleach lye for four hours at a pressure of about 22 lb. with constant circulation. The goods are then rinsed in the boiler, taken out, soured with ½ percent of sulfuric acid, rinsed again, blued if necessary, and dried. The bleach lye is made up as follows: 100 lb. of caustic soda and 50 lb. of soap or 25 lb. of Turkey-red oil are dissolved in 2000 gals. of water. In the meantime another solution is prepared of 15 lb. of sodium perborate and 12 lb. of sulfate alumina in a convenient but not excessive quantity of water. The

[10] *Ger. Pat.* 226,090.

[11] *Ger. Pat.* 249,325.

[12] For the use of magnesium perborate (and zinc perborate) as bleaching agents, see Fuhrmann, *Ger. Pat.* 250,262.

[13] Further particulars of this process are given as follows: The material is boiled-out and washed in the usual manner and then placed in the bleach bath containing for 10 gallons water, 4 ounces soap. If the water is at all hard the soap may be partly replaced by Monopol oil. The bleaching is started at 120° F. and the bath is gradually heated to 170° F.; run for 2 hours at this temperature and then heat to 200° F. for 3 hours. Wash first in lukewarm and finally in cold water. The bleach vat should be of wood with a double bottom and heated by a closed tin coil. The use of iron parts should be carefully avoided. The bleach bath should be circulated with an earthenware pump.

caustic-soda and soap solution is then mixed with the perborate solution.

Piece-goods are freed from dressing in the first place, and then well rinsed. Scouring is unnecessary except in the case of very dirty goods. The pieces are then steeped in the bleach liquor and heated in the caustic soda lye for four to five hours while the whole liquid circulates under a pressure of 22 to 30 lb. The subsequent processes are as for yarn.

Linen, ramie, and jute can be bleached by this process in weaker

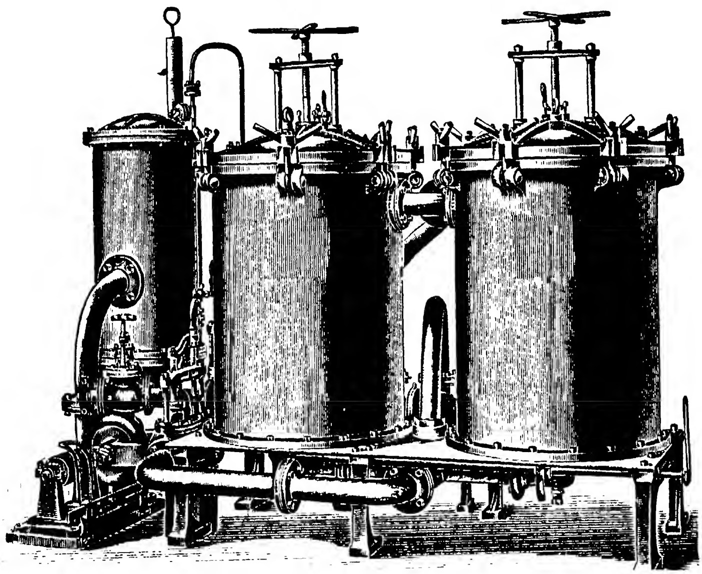


Fig. 186—Pressure Bleaching Machine for Package Goods.

lyes, or in the same lyes without artificial pressure. The advantages claimed are:

1. Saving of bleaching agent. Unscoured cotton yarn is bleached with ¾ percent of its weight of perborate.
2. Dispensing with scouring in most cases.
3. The bleach liquid is clear all the time, so that the process is suitable for bleaching cross-wound spools in machines. Baths of magnesium perborate, on the other hand, are turbid, a circumstance which makes them unsuitable for wound-up goods. Magnesium perborate is also apt to throw down magnesia soaps on the fiber, whereby the goods turn yellow on drying.
4. The presence of sulfate of alumina makes any given amount of active oxygen far more effectual in bleaching when coming from sodium perborate than it is when coming from magnesium perborate.

4. Comparison of Different Methods of Bleaching Cotton.

Of all the different processes of bleaching discussed in the preceding pages, the one which is employed to by far the greatest extent in a practical way is that involving the use of hypochlorite. The other methods, while interesting in some particular cases, are almost negligible for purposes of mill bleaching for the ordinary staple lines of cotton goods. The use of peroxide is recommended in special instances where the conditions are such that hypochlorites would be objectionable on account of the risk of injury to the material. This would only be the case, however, with very fine and delicate fabrics which would not stand properly the rather severe treatments of the hypochlorite processes.

Bleaching powder and sodium hypochlorite are the only hypochlorite compounds that have practical importance in bleaching. Bleach liquors prepared from hypochlorites of aluminium, magnesium and zinc have often been suggested and their valuable properties described in technical literature, but they have never become commercially available, as the cost is considerably higher without any compensating advantages. Considerable discussion, however, has been had concerning the relative advantages of chloride of lime and hypochlorite of soda, especially with regard to the electrolytic bleach liquors prepared from salt solution, and (in this country particularly) the chemic prepared by the solution of chlorine gas in alkaline solutions. Different bleachers apparently obtain different results in the comparison between the bleaching efficiencies of solutions of chloride of lime and hypochlorite of soda, some stating that the use of the latter effects a saving in chlorine of 20 percent; others state even as high as 50 percent. The differences are apparently due to differences in the character of the goods being bleached, as well as differences in the alkalinity and temperature of the solution. Kind and Weindel, in experiments on chloride of lime and electrolytic sodium hypochlorite, carried out under comparable conditions of the hypochlorites of sodium and calcium, found that the bleaching value of the former was about 8 percent better. These results, however, do not necessarily represent practical conditions, for it is generally conceded now that when operating under similar mill conditions the sodium hypochlorite liquors are found to be far more efficient. It has been argued, on the other hand, that this is due to the fact that the bleaching powder solutions are not used in such a manner as to develop their full bleaching activity, and that if the proper conditions are realized and maintained there can be no particular difference in any hypochlorite liquors containing the same content and concentration of active chlorine. It is claimed that under ordinary conditions (as are usually to be found in a bleachery), chloride of lime chemics are alkaline, and consequently the oxidizing effect is more slowly developed. While electrolytic hypochlorite liquors are usually in quite a neutral condition, on the other hand, the chemic prepared by dissolving chlorine gas (from liquid chlorine) in soda ash solution is quite alkaline, and yet both of these seem to possess higher bleaching efficiency than a chloride of lime liquor of the same active chlorine concentration. The

matter of comparison between different chemics is still somewhat a matter of discussion, and it is necessary to understand thoroughly the nature of the solution involved before a definite opinion can be reached. The subject is still awaiting proper scientific investigation and involves the study of the ionic dissociation of the salts involved and the hydrolysis of the alkaline bases, together with the velocity and extent of the secondary reactions involved and their reversibility. The superior bleaching effects of magnesium, zinc, and similar hypochlorite liquors is no doubt due to the absence of easily soluble hydroxides, as no doubt the presence of free hydroxide in the solution inhibits the hydrolytic

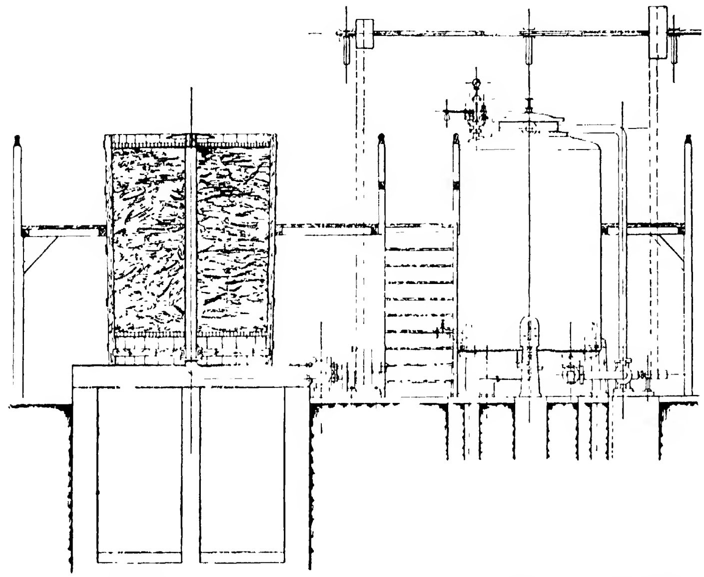


FIG. 187—Bleaching Arrangement with High Pressure Kier and Open Bleach Vat for Loose Stock or Yarns.

formation of hypochlorous acid. This is shown by the fact that when chloride of lime solutions are properly neutralized the bleaching activity is increased.

Abel also points out another possibility in this connection, and states that in the comparison of chemics from chloride of lime and sodium hypochlorite there may be a considerable difference in the diffusion properties of the solutions. In the case of chloride of lime, by the action of carbon dioxide there is formed the highly insoluble calcium carbonate:

$$Ca(OCl)_2 + CO_2 + H_2O = CaCO_3 + 2\,HClO$$

while with sodium hypochlorite there is no insoluble compound formed. Abel suggests the possibility of the insoluble calcium carbonate being

precipitated on and in the fiber with the result that the fiber substance is protected more or less from the further action of the chemic, or at least that the penetration or diffusion of the hypochlorous acid through the fiber membrane is hindered.

Ebert and Nussbaum also point out that when goods are treated with chloride of lime chemic and exposed to the air the oxidizing action of the hypochlorous acid results in the formation of hydrochloric acid and this acting on fresh quantities of hypochlorous acid liberates free chlorine; and the result will be a more severe action on the fiber. On the other hand, with sodium hypochlorite this cannot happen, as in this case the soluble sodium bicarbonate (formed by the action of the carbon

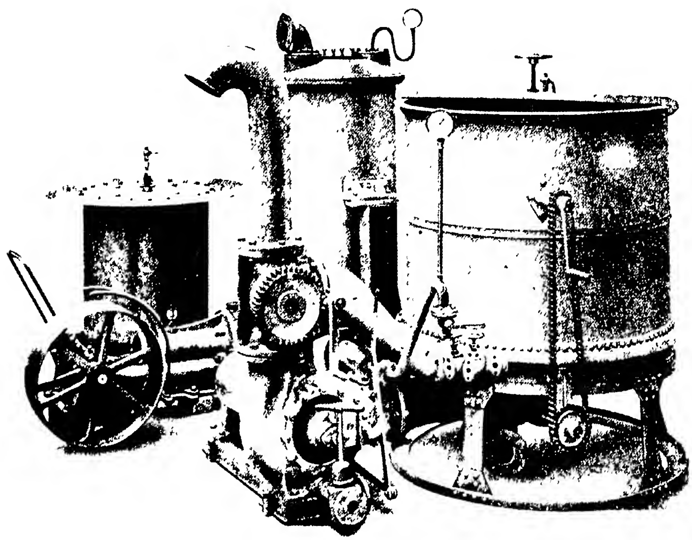


FIG. 188.—Bleaching Apparatus for Cops and Cheeses.

dioxide) is diffused equally through the liquor with the hypochlorous acid, and consequently the hydrochloric acid that is formed in the secondary reaction is immediately neutralized by the bicarbonate. From this it could be presumed that a chemic of sodium hypochlorite would be less corrosive in its action on the fiber than a corresponding chemic of chloride of lime. Furthermore, in the bleaching process with chloride of lime, the insoluble calcium carbonate is precipitated on and in the fiber and this would naturally give the goods a harsher feel than a chemic of sodium hypochlorite, as in the latter case no insoluble mineral salt is left in the fiber.

As far as theoretical considerations are involved, since bleaching is really an oxidation of the organic coloring matter of the fiber, it would seem that the value of any bleaching compound would be de-

pendent upon the amount of available oxygen to which it corresponds. The percentage of available oxygen in the four substances mostly employed in bleaching is as follows:

Chloride of lime $33\% \times \frac{71}{16}$	$= 7.5$	percent
Potassium Permanganate $O_3:K_2Mn_2O_8 = 15.2$		"
Hydrogen Peroxide 10 volumes of O	$= 1.4$	"
Sodium Peroxide 98% pure	$= 20.0$	"

The relative cost of a pound of oxygen as given by these substances, reckoned at their commercial value (1913), would be as follows:

Bleaching Agent	Cost per 100 lbs. in cents	Percentage of available Oxygen	Cost of Oxygen per lb. in cents
Chloride of Lime........ .	130	7.5	17.
Potassium Permanganate .	950	15.7	61.
Hydrogen Peroxide	430	1.4	307.
Sodium Peroxide	4000	20.0	200.

The theoretical "oxidation value" of different bleaching agents is given as follows by Kind:

100 pounds hydrogen peroxide (3 percent) = 1.41 pounds active oxygen.

100 pounds sodium peroxide (95 percent) = 19.5 pounds active oxygen.

100 pounds sodium perborate (10.4 percent) = 10.4 pounds active oxygen.

100 pounds bleaching powder (35 percent) = 7.9 pounds active oxygen.

100 pounds potassium permanganate in acid solution = 21.8 pounds active oxygen.

100 pounds potassium permanganate in alkaline solution = 15.2 pounds active oxygen.

As the action in bleaching of sulfurous acid gas is a reducing one instead of an oxidizing one, it cannot be brought into the comparison of the figures given for the cost of a pound of oxygen. From the bleaching agents above described, it is seen that peroxides are much more costly to use than either chloride of lime or potassium permanganate. These figures are, of course, based on the consideration that all of the available oxygen is utilized completely in the bleaching process. With chloride of lime, however, it is far from probable that all of its available chlorine (reckoning on 33 percent as being the average amount present in commercial samples) is utilized in the generation of oxygen. Just what the efficiency in bleaching of chloride of lime is as compared with the peroxides has never been determined. Even allowing, however, that only one-half of the chlorine is utilized in the oxidation, it will be seen that chloride of lime is still by far the cheapest bleaching agent. The peroxides probably have a greater efficiency as far as the oxidation is concerned than chloride of lime, but this efficiency would have to be

about twelve times greater than that of chloride of lime in order to make the two compare in cost.

In comparing the bleaching rapidity and efficiency of solutions of commercial hydrogen peroxide, sodium peroxide and sodium perborate, it must be borne in mind that the simple solution of these products in water in the case of the first gives a slightly acid bath, while the other two give rather strongly alkaline solutions. The degree of alkalinity of the bath materially affects its stability, velocity of bleaching and efficiency. In this connection Kind[14] has shown by a series of experiments that the more alkaline the peroxide solution the less its stability, and that in a slightly acid condition it becomes comparatively quite stable even when heated.

In calculating the oxidizing power of potassium permanganate with reference to bleaching, only three atoms of oxygen are taken as available, as the limit of deoxidation in this case is taken as the dioxide, MnO_2.

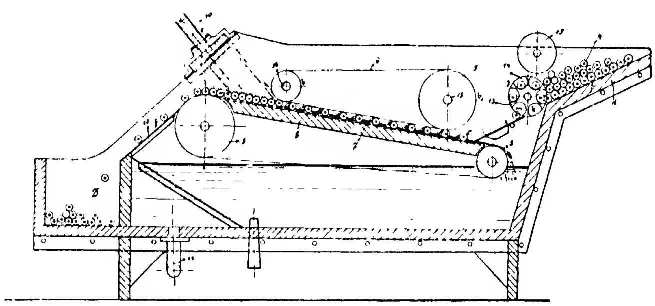


FIG. 189.—Machine for Cleaning and Reshaping Bleached Cops.

The exact efficiency of potassium permanganate with reference to its oxidizing power in bleaching is also uncertain, but it is probably much higher than that of chloride of lime, consequently, the cost of bleaching by this method should approximate closer to that of chloride of lime than does the peroxide method.

Since the bleaching of cotton (and of the vegetable fibers in general) is the result of a comparatively strong oxidizing action, it is an interesting question as to whether the bleaching only deals with the oxidation of the actual coloring matter, or if it extends to an oxidation of the entire substance of the fiber. Cross and Bevan are of the opinion that the latter is the case, and claim experimental proof of the fact.[15] As the oxidation of the fiber substance is a variable factor depending on the rapidity of the reaction and the activity of the oxygen in the bleaching medium, there may be a considerable variation in the actual consumption of oxygen in the bleaching process. As cellulose is a molecule (or aggregation of molecules) containing aldehydic (CH.O) functions, its oxidation may result in a condensation involving either

[14] *Bleichen der Pflanzenfasern*, p. 167

[15] See *Jour. Soc. Chem. Ind.*, 1887, p. 172.

a hydrolysis or an elimination of water, according to the condition under which the oxidation takes place. Rapidity of oxidation seems to favor a minimum consumption of bleaching oxygen, and the rapidity of the reaction is determined by the presence of highly active oxygen when compared with solutions of bleaching powder. Cross and Bevan are of the opinion that electrolytic bleaching liquors present the best conditions for the smallest consumption of oxygen, as in such liquors the oxygen exists in a very active condition.

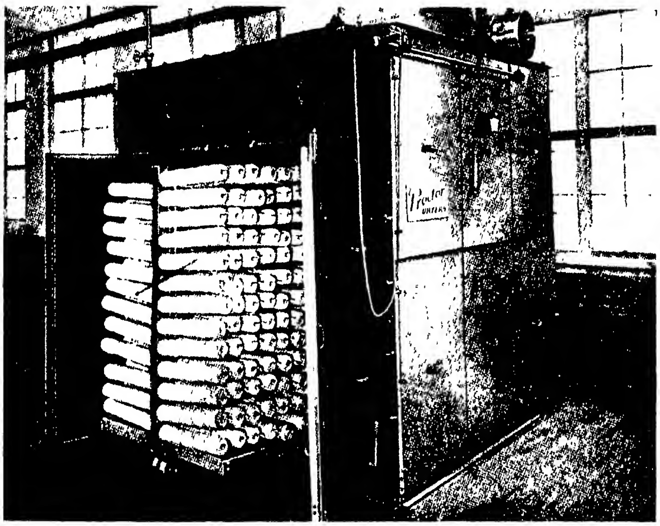


FIG. 190—Dryer for Yarn on Cones or Tubes (Proctor & Schwartz).

Some interesting tests have been made on the variation in weight, length, strength, and elasticity of cotton yarns bleached by different methods.[16] The results are summarized as follows: [17]

Process	Weight Original = 100	Length Original = 100	Strength Original = 100	Elasticity Original = 100
Boiled in water 2 hrs	..97	98	102	106
Boiled in water 4 hrs	..94	98	100	107
Boiled in water 6 hrs	. 94	98	100	102
Hypochlorite Bleach	..97	98	98	106
Permanganate Bleach	96	96	97	93
Peroxide Bleach .	93	97	92	107

It would seem from these tests that the hypochlorite bleach caused the least loss in weight, length, and strength of bleached yarns, while

[16] See Midgely, *Textile Manufacturer*, 1914.
[17] The tests were made with 2/40's carded American cotton twisted with 36 turns per inch.

the elasticity is practically equal to that of the peroxide bleach. It is interesting to note that the permanganate bleach gives the lowest elasticity, while the peroxide bleach gives the lowest strength and greatest loss in weight. These results, however, must not be taken as authoritatively established, as they would be much influenced by the methods employed in carrying out the bleaching operations.

Chapter XX.

The Bleaching of Cotton *(Cont.)*.

1. Bleaching of Loose Cotton.

Loose cotton may be bleached for several purposes: (a) for spinning into white filling yarns of medium quality, (b) for absorbent cotton for surgical purposes, (c) for packing jewelry, silverware, etc., (d) for white cotton batting for use in stuffing mattresses, etc., (e) for purified cotton fiber to be used in the manufacture of gun-cotton and artificial silk.

When bleached cotton is subsequently to be spun into yarn it is desirable to retain as far as possible the spinning qualities of the fiber, and consequently the bleaching process must be so conducted that the waxy matters are left to a great extent on the fiber, otherwise the cotton will be harsh and brittle, and will give inferior yarns on spinning, and a great deal of waste. The object in this class of bleaching is to give the cotton as white a color as possible and yet retain the natural condition of the fiber. When bleaching for the preparation of absorbent cotton, on the other hand, the main object is to remove as perfectly as possible all of the natural waxes, etc., on the fiber, and no heed is paid to the spinning qualities. Jewellers' cotton is bleached chiefly for the purpose of obtaining a white, clean, soft product which will be free from any chemical substance liable to corrode or tarnish bright silver surfaces. In bleaching for use for gun-cotton and artificial silk the purpose is to obtain a highly purified cellulose; the whitening effect is of secondary importance except in so far as it indicates the complete removal of materials other than cellulose from the fiber. For the last mentioned uses it is not necessary to employ a long fibered or high-grade cotton, and cotton waste and linters are mostly used.

Loose cotton for spinning may be bleached in the following manner: The material must first be well scoured by boiling with a solution of soda ash or caustic soda or with Turkey-red oil, as already described under the study of scouring. It is then steeped in a solution of bleaching powder standing at 2° Tw. for one hour; after which it is drained and soured off in a bath of sulfuric acid at 1° Tw. for one-half hour. It is then well washed and soaped and tinted if so desired.

In the bleaching of loose cotton or sliver which is subsequently to be spun into yarn, in order to avoid the harshness and dryness of the fiber which is detrimental to good spinning, it is advisable after bleaching to give the material a final bath containing a small amount of soap, or pass through a solution containing 3 percent of common salt or a similar quantity of glycerin and soap. This causes the fiber to retain

more moisture and consequently be softer and work better in carding and spinning. It also serves to cut down the electrification of the fiber, which is a disagreeable defect that bleached cotton readily assumes in passing through the various mechanical processes of spinning, and which results in hairy and uneven yarn.

A process which has met with considerable success is to treat the loose cotton in the so-called "vacuum" machine, which really consists of a large cast iron cylinder in which the cotton is tightly packed by a perforated cover being screwed down. The various solutions used in the bleaching are pumped through the cotton; at first warm water

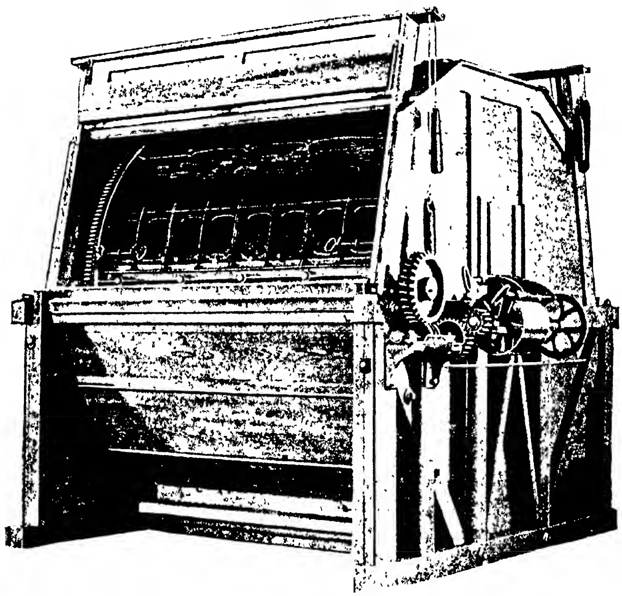


FIG. 191.—Raw Stock Bleaching Machine (Delahunty).

(which takes the place of the boiling-out with alkali), then a cold solution of chloride of lime, then sulfuric acid solution. The cotton is next washed well with cold water, soaped and tinted. This cold process of bleaching does not materially injure the spinning qualities of the fiber. The machine used may be lined with lead, though this does not seem necessary, as the surface of the iron soon becomes coated and hardened so as to resist the action of the solutions used.

The following process of bleaching loose cotton is recommended by Sansone: The well scoured cotton is worked in a bath of sodium hypochlorite containing a small amount of soda ash and standing at 2° to 4° Tw. Then it is allowed to steep for several hours, or even overnight if convenient. After removal from the bath, the cotton is

drained and washed, and then worked in a bath of sodium bisulfite at 2° Tw. Steep for about one hour, then wash well, and tint if necessary.

In the bleaching of cotton in the loose state it is found that one pound of cotton requires 15 to 25 gallons of water for all of the operations.[1]

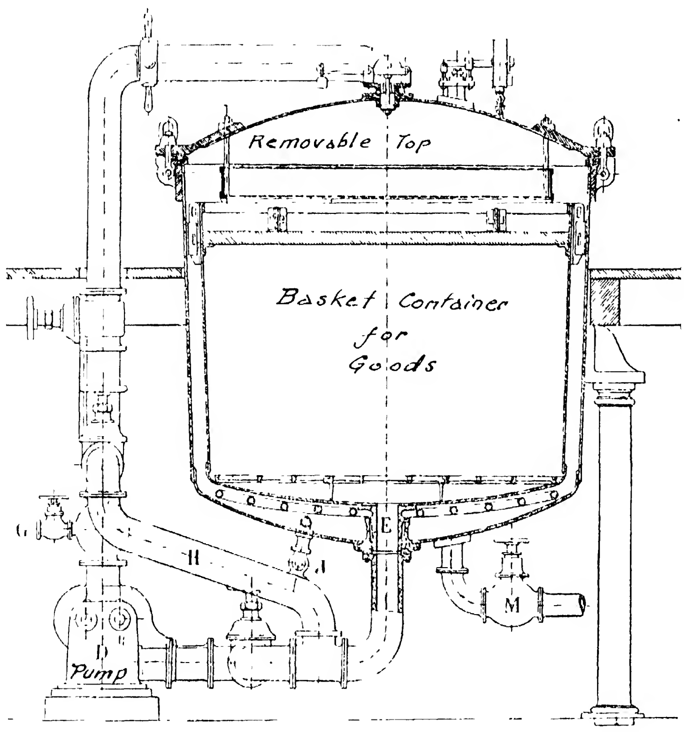


Fig. 192.—Bleaching Machine for Loose Cotton.

For the bleaching of loose cotton (especially when packed in apparatus) only the purest water should be used, especial care being taken to avoid water containing any sediment, for the cotton in this case acts as a filter and will absorb all the impurities. For the same reason in tinting bleached loose cotton it is not practical to use insoluble pigments such as Ultramarine or Indigo, as the color would all

[1] The quantity of water to be used in the different baths for the bleaching of loose cotton may vary from 10 to 30 parts for each part of cotton; the mean of this, 20 parts, is most frequently employed; and other things being the same this is always a safe quantity of water to use with loose cotton. Each pound of cotton would consequently require about 2½ gallons of water for each bleaching operation, or, more accurately, 100 lbs. of cotton would require 241 gallons of water.

be filtered out in the upper layers of the material. The same remarks are also true in the bleaching sliver or slubbing. In this case the processing is nearly always done in special bleaching machines in which the rope of fiber is closely packed, and it is essential that all the operations of boiling-out, bleaching, souring and washing should be done in the same apparatus without removing or disturbing the cotton, as otherwise the partially processed fibers would become distorted and their alignment disturbed. The apparatus, therefore, must be constructed of such materials that will make possible the use of hot

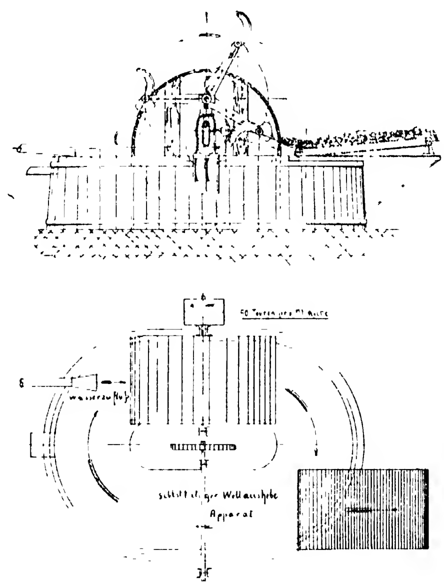


FIG. 193.—Dutch Washer for Bleaching Linters.

alkalies, as well as hypochlorite and acid liquors. Iron and copper are unsuitable for this purpose, hence it is necessary to use wood, hard lead or nickel or suitable alloys of proper resistance.

A practical method for bleaching loose cotton, card sliver, etc., is as follows: [2] The material is packed in a rectangular vat and the liquors are circulated by means of a pump, also the pipe connections and valves should be so arranged as to allow the direction of the flow of the liquor to be changed from time to time as desired. An auxiliary storage tank with proper connections should also be provided for the bleach liquors. The bleaching vat proper (which is perforated top and bottom) is surrounded by a larger tank and so connected with the pump (which is of bronze) that the liquors may be forced through

[2] *Handbuch der Färberei*, Cassella & Co.

the cotton material first in one direction and then in the other. About 1000 to 1500 pounds of cotton may be treated in one charge, and all the operations of boiling-out, chemicking and souring are conducted in the apparatus without disturbing the material. For boiling-out it is recommended to use a solution containing 2 to 3 pints of caustic soda (80° Tw.) per 100 gallons. This is introduced into the outer tank which is provided with suitable steam coils for heating. The liquor is circulated by the pump and boiled for 4 to 5 hours, after which the goods are washed twice with fresh water. The chemic consists of sodium hypochlorite of 1 to 1½° Tw., in which the material is treated for 1 hour, and thoroughly washed again. In order to insure the com-

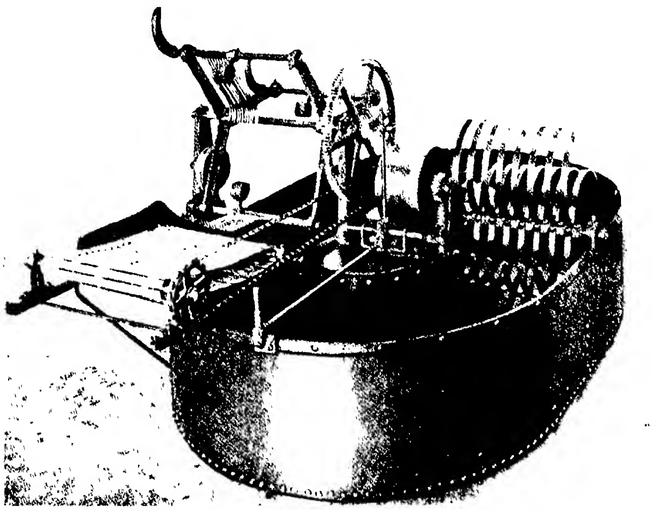


FIG. 194.—Oval Washer for Loose Cotton.

plete removal of the chlorine compounds, the hydrochloric acid bath may be substituted by one of sodium bisulfite (1 to 2 pints per 100 gallons). In bleaching sliver, cops or other form of cotton in this apparatus, it is best to introduce a layer of loose cotton above and below the other material to act as a filter to catch all sediment and impurities. For tinting the bleached cotton it is recommended to use Alizarine Cyanole FF and Alizarine Cyanole Violet R mixed in the necessary proportions to produce the desired tone.

Another method of treating loose cotton is in an apparatus similar to a Hollander. This consists of an oval tank provided with a revolving series of rakes to circulate the cotton and also with a mechanism for automatically lifting the cotton out of the liquor to a travelling apron. This apparatus is not suitable for boiling-out the cotton and this must be previously done in a kier. It is very useful, however, for

washing, chemicking and souring, and for this purpose the metal parts should be constructed of phosphor bronze. This cotton Hollander is largely used for the preparation of loose cotton used in the manufacture of gun-cotton, celluloid and artificial silk. The material is treated in much the same manner as paper pulp.

In the preparation of bleached cotton wadding the raw material is not ordinary loose cotton, but is either waste from carding or spinning, or is cotton linters, a waste recovered in ginning. The material is therefore usually very dirty and oily and requires a very thorough

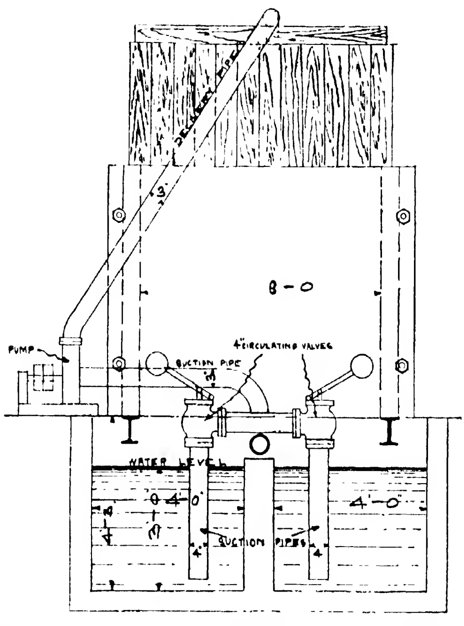


FIG. 195—Apparatus for Bleaching Cotton Linters.

boiling-out for its purification; in fact, the cleansing or boiling-out operation with alkali (3 to 5 percent of caustic soda) is the chief consideration in the treatment of this material, and the chemicking is really a secondary consideration. This is also true of the same class of material used for the manufacture of gun-cotton or artificial silk; in fact, in the latter cases the hypochlorite treatment may be entirely omitted, as the color of the fiber is immaterial as compared with the purity of the cellulose desired. For cotton wadding, however, it is desirable to have a nice white color, especially when this is used for linings, mattress material, jeweller's cotton, etc. It is customary to boil-out this material in closed pressure kiers of the usual type, though when large installations are in question the kier is provided with a suitable ar-

rangement for the easy removal or evacuation of the product. If there is much mineral oil present in the fiber (from machine lubrication) it is well to add to the boil-off liquor some soluble oil as an emulsifier, or a solvent such as ethylene perchloride (b. p. 121° C.). This is especially to be observed in the preparation of cotton waste for nitration. If the usual form of kier is used for boiling-out, the material must be bleached and soured in other apparatus, for which purpose the cotton Hollander is well adapted. In some cases, however, the installation is so arranged to conduct all the bleaching operations in one machine, in which case a special apparatus is required similar to one of those already described. The chemicking and souring and washing operations are conducted in the usual manner. It is sometimes re-

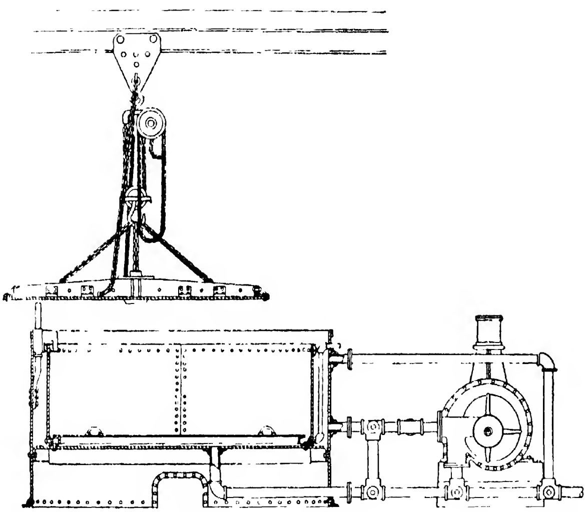


FIG. 196.—Machine for Boiling-out and Bleaching Raw Cotton for Spinning.

quired to give the bleached cotton wadding a scroop or crunch. This is usually done by treating with a bath containing 3 percent of neutral soap and then souring in a bath of acetic acid (or sulfuric acid) so as to precipitate free fatty acid in the fiber. Also impregnation with lime salts or alum have also been used. The bleached wadding is also blued or tinted with Indigo Carmine or soluble Prussian Blue.

2. Bleaching of Cotton Linters.

Cotton linters are often bleached for the purpose of obtaining a pure cellulose fiber and destroying and removing the motes, seed particles, fatty matters, dirt, etc. Owing to the very short staple of linters the boiling-out and bleaching processes must be conducted in such a manner as to prevent undue loss of fiber. The main feature in bleaching linters is a very thorough boiling-out with caustic soda liquor

under considerable pressure, as by this means alone the motes and seed-hulls can be effectively softened and decomposed. This is followed by a treatment with either acid or chloride of lime for the purpose of further decomposing the motes and converting them into soluble products or into a powdery condition so that they may be washed away from the fiber. In case a white fiber is desired chloride of lime must be employed, but if the color is not an essential feature then the acid treatment alone will often suffice. Bleached, or rather purified, linters are largely employed as a basis of nitrated cotton for gun-cotton and for the various cellulose solutions. Such solutions, for example, are the collodion solutions in ether-alcohol employed for the spinning of artificial silk by the Chardonnet process and the cuprammonium solutions of cellulose used for the spinning of cuprate silk.

For the bleaching of cotton linters a high pressure boiling kier is necessary with outside circulation and centrifugal pump to work at 20 to 40 pounds pressure. The following solution is used for boiling-out: 2 percent of caustic soda, ¼ percent of sodium silicate and ¼ percent of tallow soap. The cotton is boiled for 2 to 3 hours at 20 pounds pressure; the steam is then shut off and the circulation continued for 3 hours longer. The steam is then blown off and the material well washed in the kier. The stock is then put into a bleaching cistern (see Figure 192) and treated with chloride of lime liquor at 1° Tw. The cistern is provided with a pump to circulate the bleaching liquor which is introduced on the top of the cotton, then passes down through the mass and collects in the well at the bottom, from which it is again pumped to the top of the tank. The goods are treated with the bleach liquor for 3 to 5 hours according to quality. The cotton is then washed well and then soured with muriatic acid at 1° Tw. for 1½ hours. It is then washed thoroughly until the last trace of acid is removed.

In Europe, where large quantities of bleached cotton waste or linters are used for the preparation of artificial silk (by the cuprate process) the Kuhn system has been quite extensively used. This consists of a special installation for boiling-out under high pressure (about 57 pounds), and for washing, chemicking and souring in special kiers provided with arrangements for automatically handling the material.

3. Preparation of Absorbent Cotton.

In the preparation of absorbent cotton for surgical purposes the main object is to obtain a product which is absolutely clean and highly absorbent. While the usual methods of cotton bleaching are employed certain precautions have to be observed in order to obtain a highly purified product. It is essential that no substances be present that may cause irritation in a wound, and furthermore it is necessary that the cell-wall of the cotton fiber be made as porous as possible. The chief process in the preparation of absorbent cotton is a very thorough boiling-out with alkalies so that the fiber may be freed in the most complete manner from all waxy, resinous, oily and albuminous substances which exist as natural or accidental impurities in the cotton. As a rule, stronger solutions of caustic soda are employed than when the

cotton is bleached for purposes of spinning. The boiling-out operation is conducted in a closed kier under a pressure of 2 to 3 atmospheres (corresponding to a temperature of 250 to 270° F.). A solution of caustic soda of 2 to 4° Bé. is employed and the boiling is continued for from 5 to 10 hours. The caustic soda treatment also destroys the small particles of seed and "shives" which are apt to be found in considerable quantity in the kind of cotton which is usually bleached in the loose condition. The operations of boiling-out and bleaching loose cotton cause the material to become greatly matted together, especially if it is worked by hand. By using machines, however, the fiber may be kept

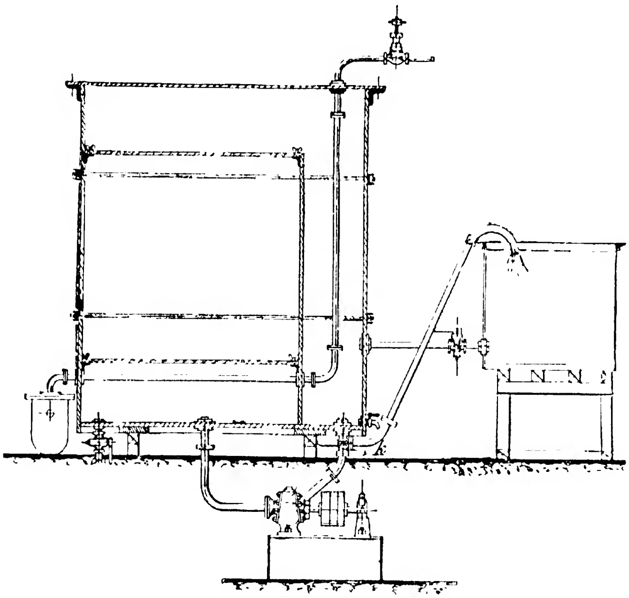


FIG. 197—Apparatus for Bleaching Loose Cotton.

in much better condition; though as most machines necessitate the use of copper or bronze parts, the precipitation of copper compounds in the cotton, which would render it unfit for use for absorbent purposes, should be guarded against by suitably observing certain precautions. Caustic soda attacks copper surfaces very readily, forming a hydrate of copper; this is readily dissolved by the acids generated in the bleaching with chloride of lime, and as a result the cotton becomes impregnated with a salt of copper. If the cotton is soured off with sulfuric acid after the treatment with the bleaching powder, an insoluble double sulfate of lime and copper will be precipitated in the fiber, which cannot subsequently be completely washed out. If, however, hydrochloric acid is used for the souring bath, no insoluble compound will

be formed, and the copper salt may easily be washed from the cotton subsequently.

The bleaching proper of absorbent cotton is conducted in the usual manner for cotton bleaching, though it is much more desirable to use sodium hypochlorite than chloride of lime, in order to avoid the forma-

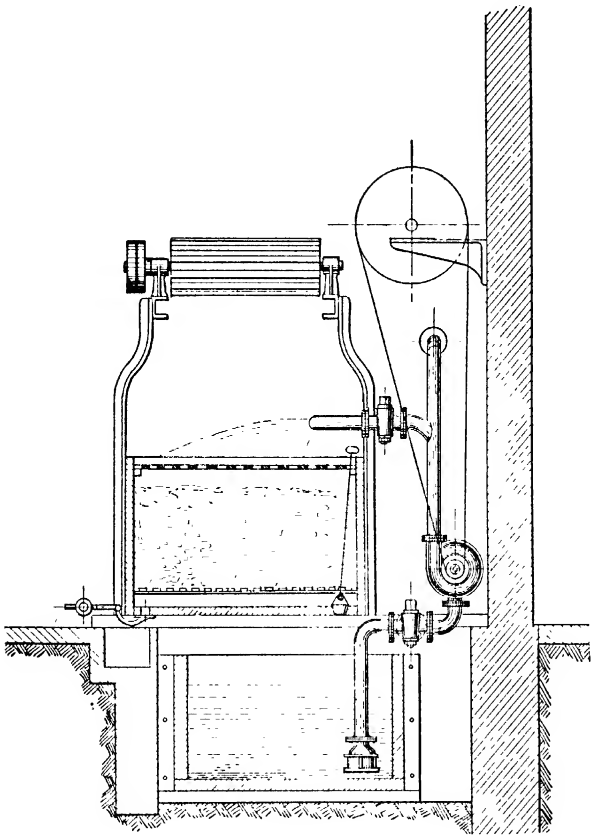


FIG. 198.—Bleach Vat for Warps and Skeins.

tion of insoluble lime compounds which would tend to lessen the absorbent property of the product.

Kilmer recommends that absorbent cotton should be made from the type of cotton known as Texas strict middling, as other grades give inferior results. In Europe the better grades of absorbent cotton are made from Egyptian comber waste, while in this country peeler comber waste is largely used, as this product is quite clean and free

from motes and seed particles.[3] The lower grades of absorbent cotton, and especially that used for sponging, is made from the cheaper grades of cotton waste and consists of shorter fibers and shows the presence of many nibs of short felted fibers.

According to Kilmer, absorbent cotton should be bleached in accordance with the following procedure: Washing in water; alkaline hydrolysis, consisting of a boil with a 1 percent solution of caustic soda for 12 to 48 hours under low pressure; washing; bleaching with sodium hypochlorite (the action being prolonged and the solution containing 0.01 percent of available chlorine); hydro-extraction; souring with a 2 percent solution of sulfuric acid; washing and hydro-extraction; a second alkaline hydrolysis consisting of a short boil with 0.25 percent caustic soda; washing and hydro-extraction; a second acid treatment; prolonged washing; treatment with antichlor (bisulfite or hyposulfite of soda) or a solution of soap; final washing. Sterilization by steam or formaldehyde gas is also employed in some cases. The dried bleached cotton is carefully and thoroughly carded and made up into thin laps which are rolled and cut into convenient sizes. A good quality of absorbent cotton should be capable of taking up from 18 to 20 times its own weight of water. A small pellet of the dry cotton when thrown on the surface of cold water should sink almost immediately.[4] When bleached with sodium hypochlorite solutions absorbent cotton will not give more than 0.05 percent of ash on ignition, but when bleached with chloride of lime the ash will usually be from 0.15 to 0.30 percent. Absorbent cotton will nearly always show the presence of considerable oxycellulose and will have a harsh crackly feel due to the acid treatments to which the fiber has been subjected. It is not good policy to soften the fiber by treatment with soap solutions or cotton softeners, as these detract from its absorbent properties and are liable to produce yellow discolorations on storing. A well prepared absorbent cotton should not deteriorate with age if properly packed; if lime salts or soaps, however, are left in the fiber deterioration is very liable to occur. In the preparation of absorbent cotton it is very essential to employ as soft a water as possible and the washing after each treatment should be very thorough.[5]

4. Bleaching of Cotton Yarn.

Yarn may be bleached in a variety of forms, (1) as cops, (2) as spools or cheeses, (3) as beamed warps, (4) as warps in rope form, and (5) as skeins. Heretofore it was in the last two forms that yarn was mostly processed, both for bleaching and dyeing; but during

[3] In Europe an unbleached absorbent cotton is largely used which is made by a simple extraction of the fatty matters from the fiber by the use of volatile solvents.

[4] The U. S. Pharmacopœia gives the following requirements for absorbent cotton under the head of "Purified Cotton": White, soft, fine filaments, appearing under the microscope as hollow, flattened and twisted bands, spirally striate, and slightly thickened at the edges; inodorous and tasteless; insoluble in ordinary solvents, but soluble in an ammoniacal solution of cupric oxide. When Purified Cotton, previously compressed in the hand is thrown on the surface of cold water, it should readily absorb the latter and sink, and the water should not acquire an acid or an alkaline reaction (evidence of proper purification and absence of fatty matter). Purified Cotton should be perfectly free from all visible impurities, and on combustion should not leave more than 0.3 percent of ash.

[5] Water of zero hardness obtained by means of a Zeolite softener is probably the best kind of water to use for the preparation of absorbent cotton.

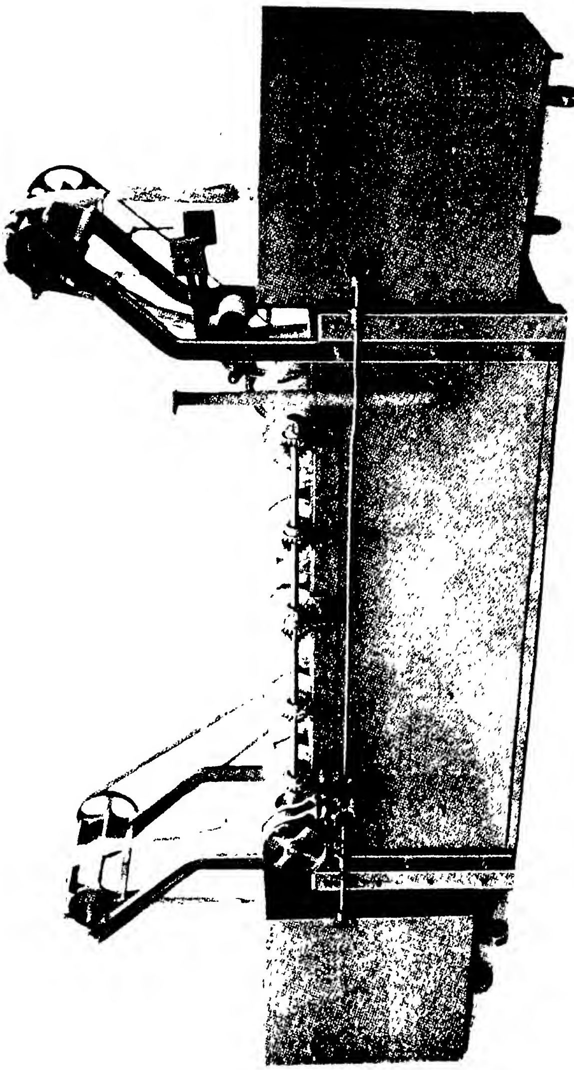


FIG. 199.—Machine for Bleaching and Washing Skeins Tied in Long Chain.

recent years there has been great activity in the construction of machinery suitable for the dyeing and bleaching of yarn in the package form. It may readily be seen that if the various processes may be properly carried out and satisfactory results obtained it becomes much more economical to bleach yarn in the package form (cop, spool or beamed warp), as in this manner reeling and winding are avoided with the labor and waste they entail. The possibility of taking cops directly from the spinning mules, bleaching them and then using them straight

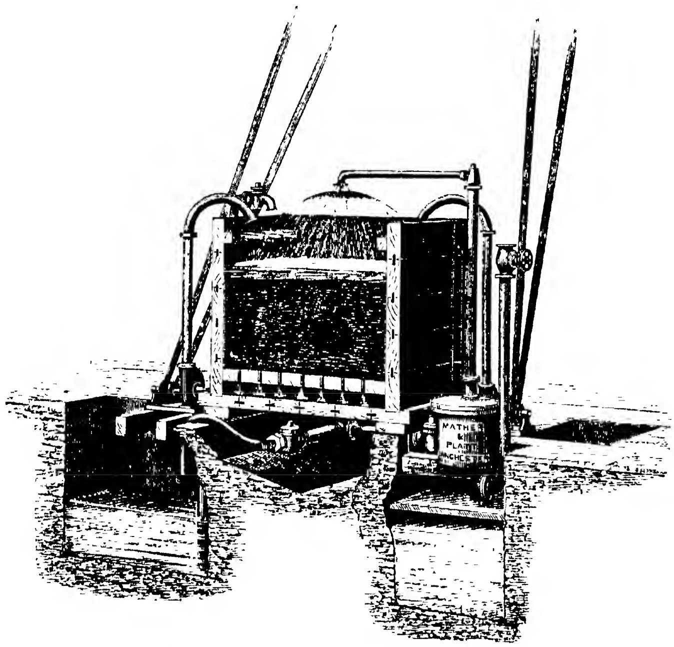


FIG. 200.—Yarn Bleaching Apparatus.

away as filling yarns in weaving has long appealed to the practical manufacturer as a highly economical proposition. Certain difficulties, however, have long acted as a deterrent; the uniform and thorough impregnation by the necessary solutions of the yarn in the cop form has long been a serious problem and has required the development of special forms of circulating apparatus; the fact that the cops (or in fact any compact package of yarn) act as a filter on the various liquids, and even the water has also been a factor that generally led to defective results; the proper drying of the cops was also a problem which presented many difficulties.

Yarn spun on ring frames is not obtained in the form of cops, but as bobbins on a wooden holder which was not adapted to use in bleach-

ing machines. Such yarn, however, was wound on spools or tubes which could be bleached. In fact, though spools (cross-wound) form a much thicker and bulkier package, and contain more yarn than cops, they can be penetrated by liquids much easier, due to the fact that the cops are built up by running the yarn in close and compact winding, while the tubes are built up by winding the yarn in criss-cross layers so that the structure of the tube is porous or cellular with appreciable interstices between the warps of the yarn. Cheeses are large tubes in the shape of a truncated cone built up in the same way.

Beamed warps make a convenient package for handling warp yarn. The warps are made up directly from the spools or bobbins and may be beamed on a perforated cylinder adapted for use in a special form of bleaching machine, and forms a single large package which may be

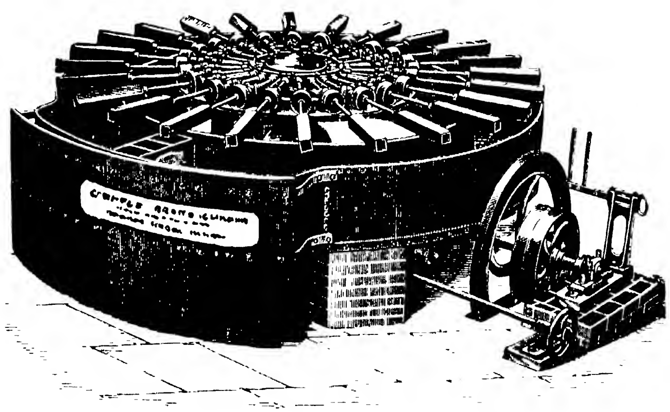


FIG. 201.—Scouring and Washing Machine for Yarns.

conveniently and economically handled. All the difficulties which have been mentioned in connection with the bleaching of cops also pertain in greater or less degree to the treatment of tubes and beamed warps.

Machine bleaching of yarn in package form has been carried out to considerable perfection in Europe, both on the continent and in Great Britain. In America, however, progress in this line has been very slow, and bleachers here have been very shy in trying out the new methods and in devising various schemes to overcome the difficulties encountered. This is indeed rather surprising owing to the highly developed mechanical skill of the American engineer and the tendency of most manufacturers in this country to adopt the use of suitable machines wherever possible for the handling of goods.

5. Bleaching of Cotton Skein Yarn.

The bleaching of cotton in the condition of skein yarn is carried out in general in the same manner as that of loose cotton, except that

the manner of handling is somewhat different. The scouring with caustic soda is usually effected by boiling in kiers, which may be either open, or of the closed low pressure type. These kiers consist of large iron cylinders which are best lined with cement. The entire top is removable and may be screwed down tightly by means of a number of clamps. The hanks of yarn are twisted and packed in systematically; the liquor is then run in from the top, after which the lid is screwed down. The steam is introduced through the bottom of the kier and

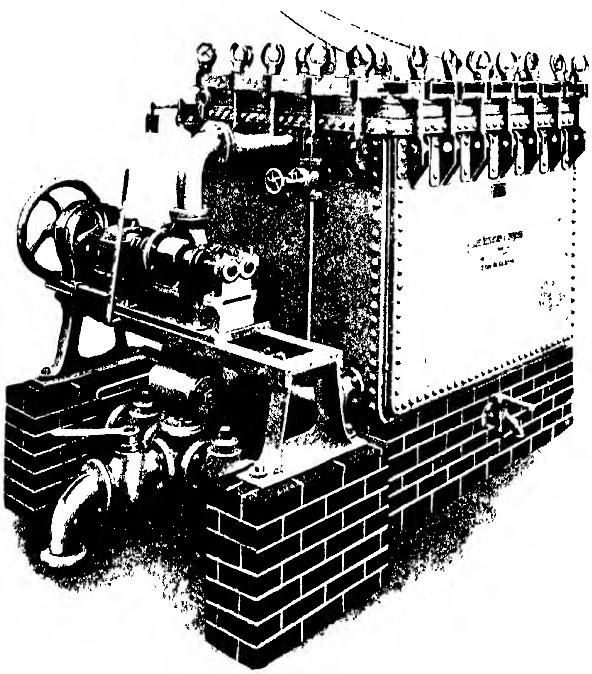


FIG. 202.—Bleaching Apparatus for Boiling-out, Chemicking, Souring, and Washing Skein Yarns and Warps.

passes up through an injector in the middle of the kier to the top. This causes a thorough circulation of the liquor through the material. After several hours' boiling, the liquor is drained off, the cotton removed and steeped in a bath of chloride of lime which is from 2° to 4° Tw. After steeping for one to two hours, the yarn is removed, rinsed off, and soured in a bath of sulfuric acid at 1° Tw., after which it is thoroughly washed and soaped. The bleached yarn may be tinted in the soap bath by adding such coloring matters as Ultramarine, Methyl Violet, Methylene Blue, etc. Care should be taken to wash the material very thoroughly, as if a trace of acid is left in the cotton, on

drying the yarn will be tendered. The soap has the purpose of neutralizing any remaining traces of acid, and also softens the cotton. Instead of scouring in caustic soda, a boiling bath of soda ash may be

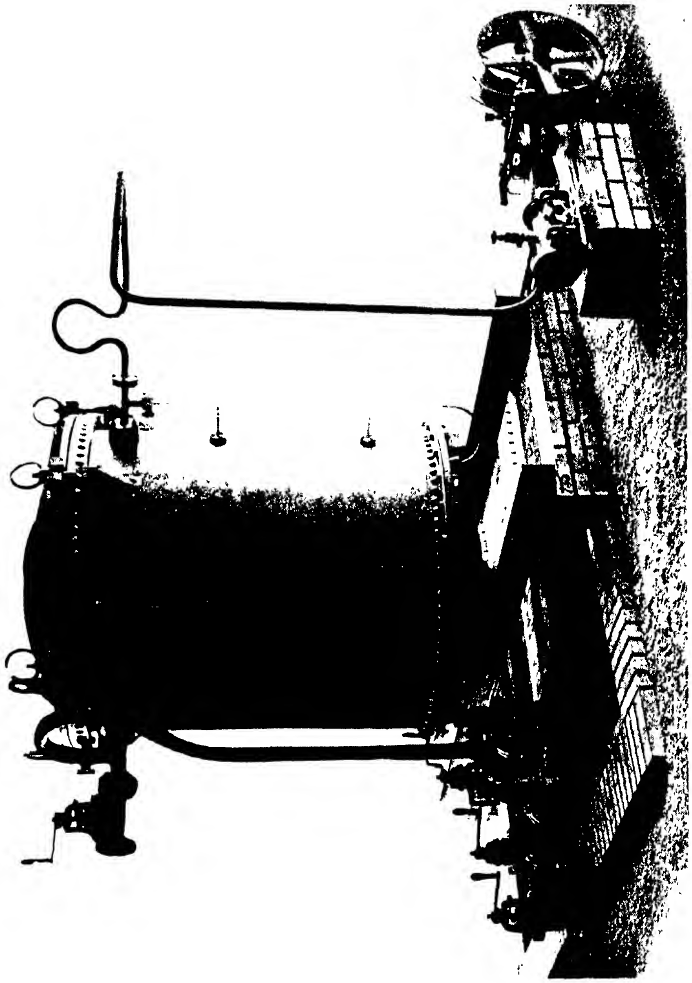


FIG. 203.—Vacuum Bleaching Apparatus for Fine Yarns.

used, or the cotton may be scoured out by the use of Turkey-red oils. Scouring by means of a boiling bath of milk of lime in low pressure kiers has also been used, but the favorite practice at present is to use the caustic soda process.

By the use of specially constructed tanks for the purpose of bleaching, souring, and washing the yarn considerable hand labor may be saved. Such an arrangement is as follows (see Figure 198): The yarn is packed in a cement or wooden cistern provided with a false bottom; the liquor is pumped up from a lower tank to the top of the yarn and is allowed to trickle through the cotton in an even and systematic manner; after percolating through the yarn, the liquor collects in the lower tank again, and is pumped back through the goods. One tank may be

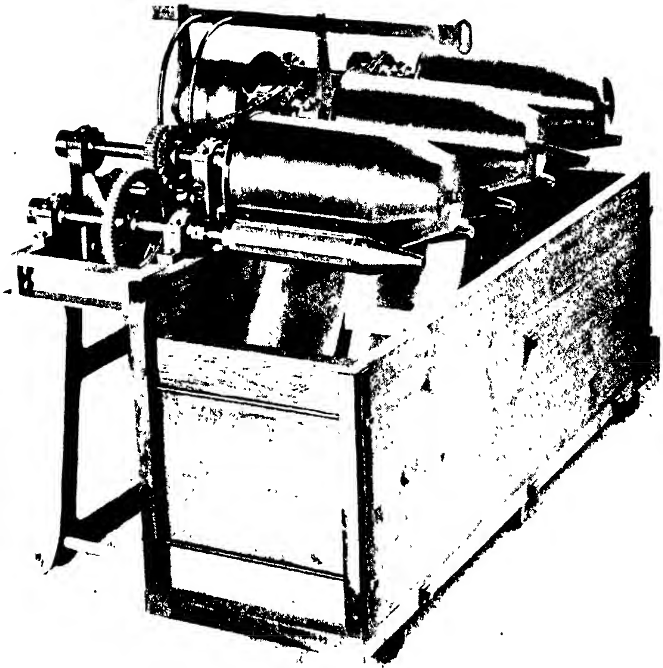


FIG. 204—Skein Yarn Washing Machine.

used for the several operations of bleaching, souring, washing, and soaping without removing the cotton.

Mather & Platt have constructed an apparatus in which all of the operations, including the boiling in alkali, may be carried out without removing the yarn (see Figure 200). The apparatus consists of a wooden tank with a false bottom. The yarn is packed in evenly, and boiling caustic soda lye is caused to circulate through the material by means of a steam injector, which draws the liquor up from below the false bottom and sprays it over the top of the cotton. After being boiled for some hours, the lye is run off, and the goods are washed

with water. Next follows the treatment with the solution of bleaching powder, which is drawn up from a submerged tank and sprayed over the cotton by means of a pump. The treatment with acid, and the washing and soaping are carried out in the same manner.

A typical summary of the operations of yarn bleaching is given as follows:

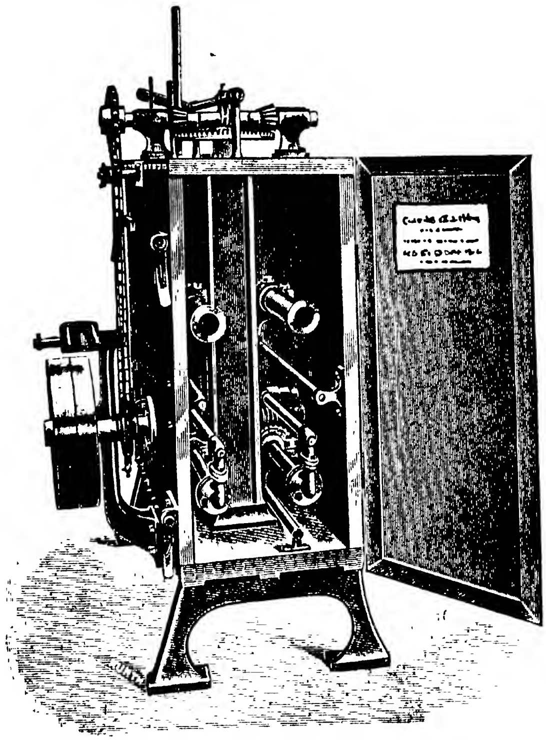


FIG. 205.—Stretching and Lustering Machine for Bleached Mercerized Yarns.

1. Boil 8 to 10 hours in a 5-lb. pressure kier with 4 percent of soda ash (or the same amount of caustic soda).
2. Wash in open tank, give two turns.
3. Treat for 6 hours in a circulating cistern with a solution of bleaching powder at 2° Tw.
4. Wash in same cistern for 10 minutes.
5. Sour in same (or other) cistern for 15 minutes with sulfuric acid of 1° Tw.
6. Wash in cistern with three changes of water.
7. Soap off, hydro-extract, and dry.

If iron stains develop on the cotton after the treatment with chloride of lime, instead of using sulfuric acid for souring off, hydro-

chloric acid should be employed, as this more readily dissolves off the iron. The density of the hydrochloric acid bath should be the same as that of the sulfuric acid.

It is said that by adding a small quantity of soap to the caustic soda in the lye boil, the scouring of the cotton is greatly facilitated. The same is also true of the addition of soluble oils or ricinoleate soaps.

If the yarns operated upon are of very hard twist, it may be necessary to repeat the operations of bleaching one or more times in order to obtain a perfect white.

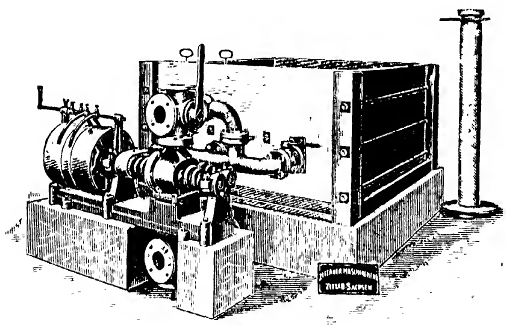


FIG. 206.—Bleaching Apparatus for Beamed Warps.

Where it is desired merely to bleach small amounts of cotton yarn, and the proper kiers and cisterns are not available, the following process is recommended as giving good results:

1. Boil for two hours in a bath containing 2 percent of soap and 1 percent of caustic soda.
2. Wash in fresh water.
3. Steep for two hours in chloride of lime at 2° Tw.
4. Wash in fresh water.
5. Sour in sulfuric acid at 1° Tw. for one hour.
6. Wash in two changes of water.
7. Soap in 1 percent of soap for one hour, tinting at the same time if so desired.

Yarn that is intended to be dyed immediately after bleaching generally is not soaped off, nor is it tinted. If it is to be left in the white condition, however, it is soaped and tinted. The soaping and tinting may be carried out in what is known as a "dumping" machine. This consists essentially of two wooden rollers, the upper one being covered with cotton rope and resting with its own weight on the lower one. The hanks of cotton yarn linked together in chain form after being bleached are steeped in the soap solution containing the blue for tinting, and then passed rapidly between the rollers of the dumping machine; the irregularities caused by the linking of the hanks of yarn

or the plaiting of the warps, gives a constant jumping motion to the upper roller and this beats the liquid thoroughly into the fiber so that the impregnation is very complete. If the yarn is washed in other washing machines in separate hanks, the pounding or "dumping" may be done in what is known as the "stocks" in which the yarn saturated with the soap liquor is pounded by a wooden hammer.

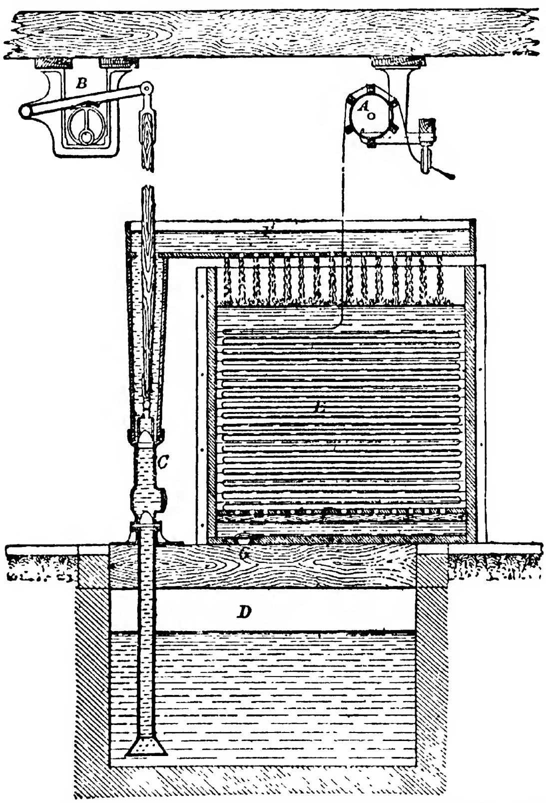


FIG. 207.—Apparatus for Chemicking, Souring and Washing Warps.

6. Bleaching of Cotton Warps.

In the bleaching of cotton warps a variety of processes may be employed, depending mostly upon the mechanical manipulation selected for the running of the warps. In most cases the warps are boiled-out in the same manner as skein yarn in closed kiers, the warp yarn being run in rope form and plaited down in the kier. The boiling-out is conducted in the same manner as with skein yarn as to manner of treatment and chemicals employed. Besides being processed in the

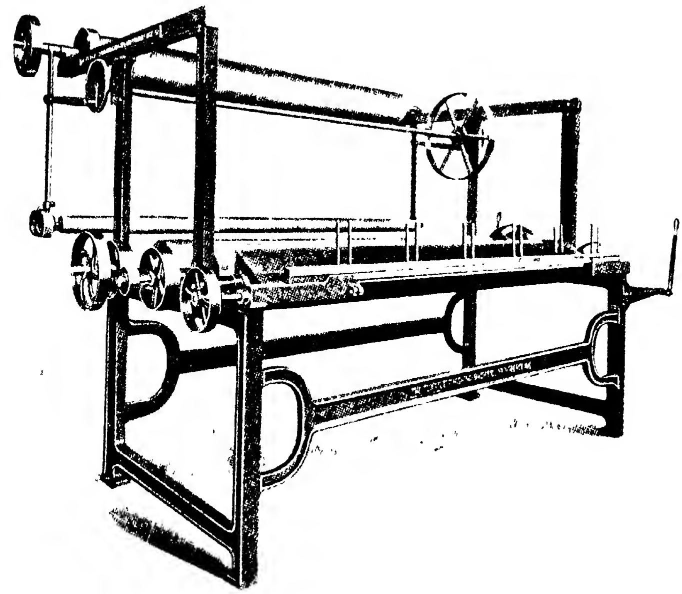


FIG. 208.—Warp Splitter (Text. Fin. Mchy. Co.)

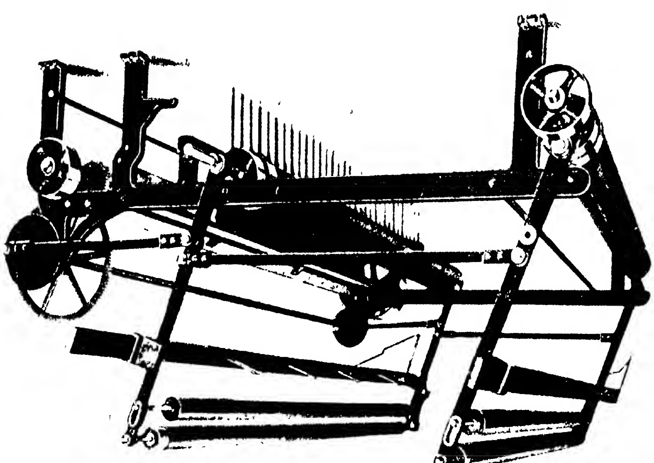


FIG. 209.—Overhead Warp Splitting Machine (Text. Fin. Mchy. Co.).

rope form the warps may be suitably doubled on a special machine for this purpose, or they may be linked up in a chain form, the links consisting really of loose ties, which may be done either by hand or by a special machine.

In the operations of chemicking and souring, several methods of running may be used. In the still bleach process, the warps are laid down in a tank which may be of either wood or cement, and the various bleach liquors are circulated through the material by pumping in at the top, and draining down by gravity. This method is quite

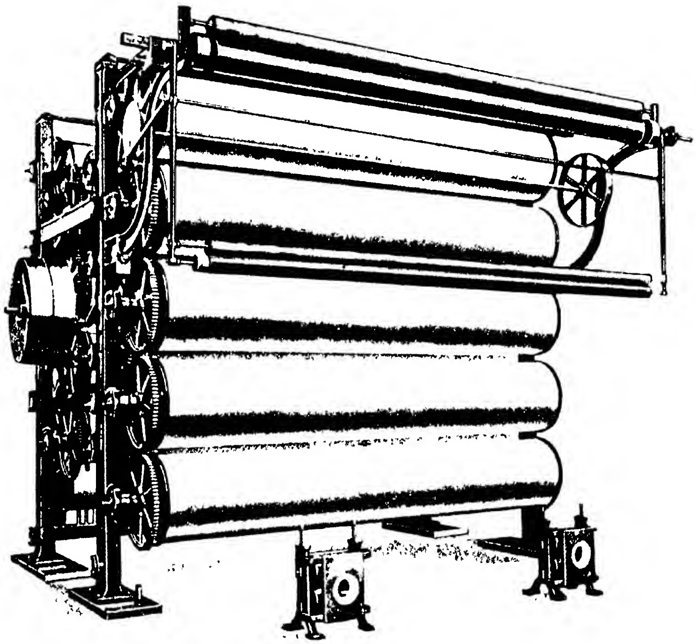


FIG. 210.—Eighteen Cylinder Warp Drying Machine (Text Fin. Mchy. Co.).

extensively used, but care must be had to have the warps so packed in the tank that undue channeling of the liquid is avoided, otherwise uneven results will be obtained. Also in this method the goods act as a filter towards the solutions employed, and it is necessary to use clean pure liquors on this account. Another method is to run the warps in rope form through a machine consisting of a series of tanks or boxes, provided with suitable guide rolls to carry the material up and down through the solutions in the several tanks, and also having squeeze rolls between the tanks. In this system the warps may be bleached in a continuous manner, running through the machine without interruption in the process. In some cases, even the raw warp without previ-

ous kier boiling is used, the first few boxes of the apparatus being used for boiling the goods in caustic soda and washing. The warps are then run through a solution of hypochlorite, then given a rinse in water, then a sour and another rinse, then finally run through a soap and finish bath. The warps must be run at a low speed and be given sufficient contact with the respective solutions to efficiently bleach the cotton. By this means a very uniform bleaching may be obtained and a large production put through. It is necessary, of course, to con-

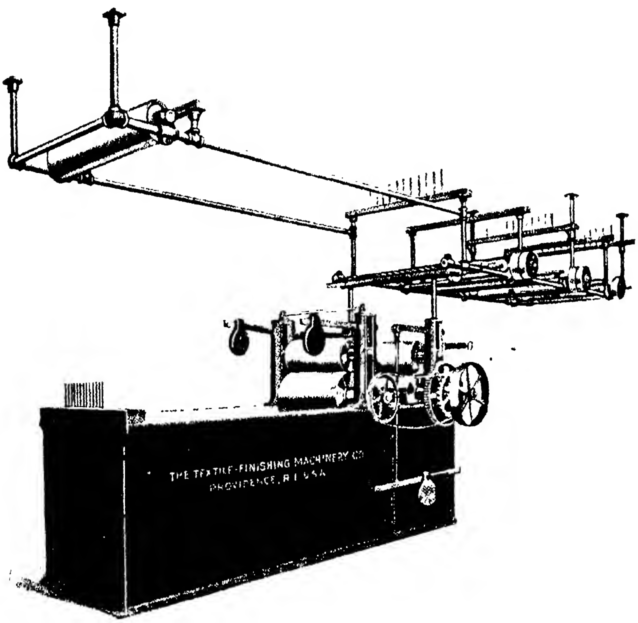


FIG. 211.—Warp Boiling-out Machine (Text. Fin. Mchy. Co.).

stantly freshen up the various liquors in the different boxes so as to maintain them at practically a uniform strength.

Another method which is employed to quite some extent is to run the doubled warps through the chemic liquors in a single or double compartment machine provided with guide rollers and squeeze rollers; or an ordinary form of the so-called Scotch dyetub may be used. After passing through the squeeze rolls the warps are piled up in boxes or in a cement bin. The squeeze rolls of the machine are so adjusted as to leave the proper amount of the chemic in the yarn, and the bleaching action is brought about by leaving the warps exposed in the piles for several hours. After this they are run through a similar machine for the purpose of washing, souring and finishing.

A long string-tub machine may also be used for bleaching warps. This machine consists of a long tub or tank provided with a reel and a set of wooden squeeze rolls. The warp in rope form enters at one end of the machine and passing up and down over the roll and through the squeeze rolls and guide pins, progresses spirally towards the other end of the apparatus. This method of treatment allows of the goods being given quite a prolonged treatment in the liquors. By linking up several such machines in series the warps may be run so as to give a continuous bleach by this process. Or after coming from the string-tub machine the warp may be folded down in boxes and allowed to age until sufficiently bleached, and then run through similar machines for souring, washing and soaping.

By whatever process the warps are run the general treatment is the same. In a continuous system, as a rule, it is necessary to employ stronger solutions than when the goods are saturated with the chemic and then folded down in boxes for ageing. In the latter case care must be had to avoid drying of the warps in spots, as this will lead to tender yarns and defective bleaching. Usually the warps are suitably tinted with a bleacher's tint in the final soap or softening bath and then run through squeeze rolls and over drying cans. If the warps have been doubled or linked they must be run through a warp splitter or an apparatus for unlinking before passing over the drying cans.

Chapter XXI.

The Bleaching of Cotton Cloth.

1. General Considerations.

As already stated, this may be of three kinds, according to the purpose for which the cloth is afterwards intended:

(a) Market bleach, for goods to be left in the white.
(b) Madder bleach for dyeing of Turkey Red.
(c) Printer's bleach for cotton cloth to be printed.

The only difference between the various bleaches is the degree to which the bleaching action is conducted. There is no essential difference in the nature of the process itself.

The following is an outline of the various operations through which cotton cloth must pass in order to obtain a satisfactory bleach:

OLD METHOD	NEW METHOD.
1. Singeing.	1. Singeing.
2. Steeping.	2. Steeping (often omitted).
3 Boiling with lime under pressure.	3 Caustic soda boil under pressure
4. Souring with weak acid.	4 Treatment with hypochlorite.
5. Boiling with resin soap.	5. Souring with weak acid
6. Boiling with soda ash.	6. Washing and soaping.
7. Steeping in chloride of lime.	
8. Souring with weak acid.	
9. Washing and soaping.	

These different operations may be varied considerably in different mills, or other methods of treatment may be substituted; but in general, it may be said that a singeing, scouring, bleaching, souring, washing, and soaping are embodied in all of the processes leading to a complete bleaching for cotton cloth. Between the various processes it is also understood that thorough rinsings have to be given the cloth.

For goods that are to be sent into the market in the white condition, the singeing operation is frequently omitted, and the boiling is sometimes carried out in low-pressure kiers, and instead of resin soap in the first lye-boil, soda ash or caustic soda is used. In some mills it is the practice to give another lye-boil after the goods come from the chemic or solution of bleaching powder or hypochlorite. Goods intended for the market bleach must also pass through a series of careful finishing operations after the bleaching proper, such as starching, filling, steaming, beetling, calendering, etc. The madder bleach was so called because it was intended for goods to be subsequently dyed or printed with madder; in place of madder, alizarines are at

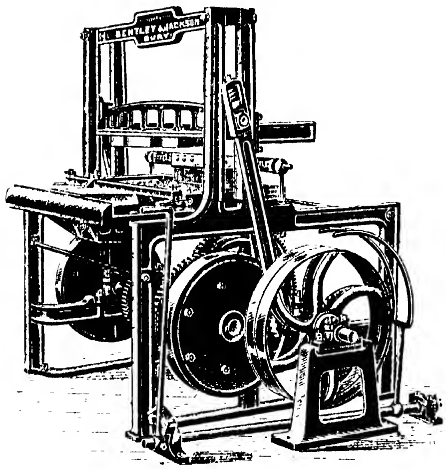


FIG. 212.—Machine for Marking Cloth.

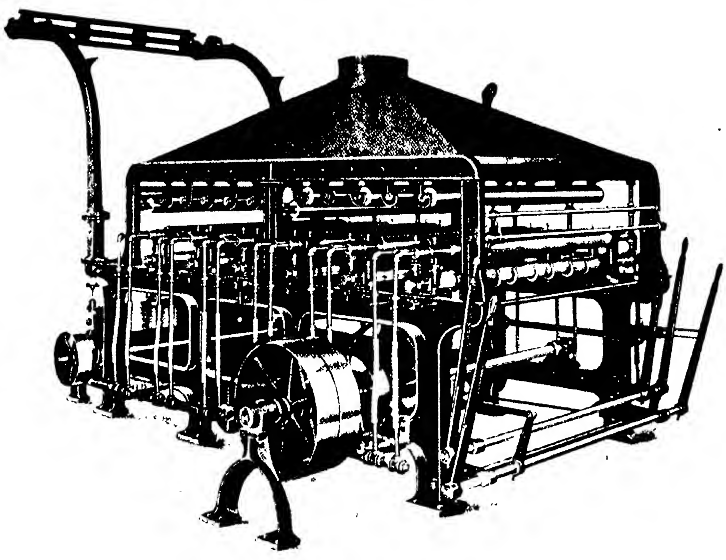


FIG. 213.—Six Burner Singeing Machine (Text. Fin. Mchy. Co.).

the present time employed for the production of Turkey Red. It has been found that the best results with this color cannot be obtained unless all the impurities in the cotton are completely removed, hence bleaching for this purpose must be very thorough.

In cotton cloth, besides the natural impurities present in the fiber itself, there is nearly always more or less sizing material, grease, and dirt from the weaving, etc.,[1] which also have to be removed in the bleaching; hence the problem is somewhat more complex than with yarn bleaching.

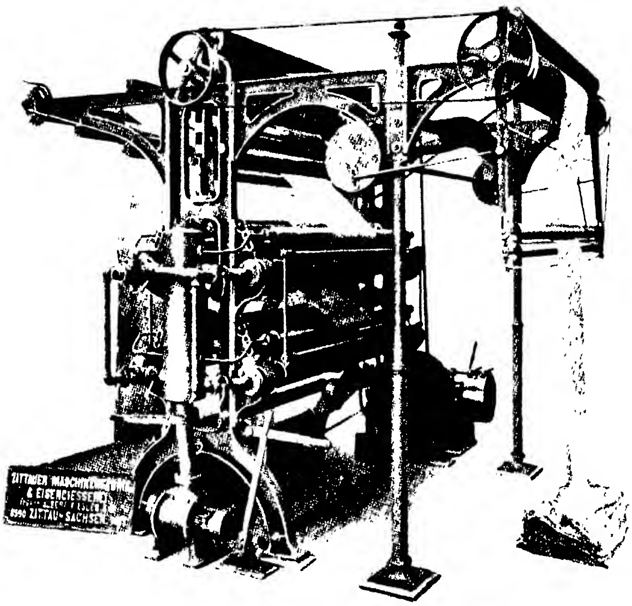


FIG. 214.—Singeing Machine (German Type).

2. Marking and Stitching.

The first process which the cotton pieces pass through preliminary to bleaching is marking[2] and stitching; the several pieces varying from 50 to 100 yards in length are stitched together by means of special sewing machines, and certain marks are also placed on the pieces in order that they may be subsequently identified for one reason or another. After stitching and marking, the pieces are then rolled up in large bales containing several thousand yards but not too large to be inconvenient in handling.

[1] The foreign materials to be eliminated in the bleaching of cloth are as follows:
(a) Sizing, including glue or gelatine, starch, albumen, sugar, and gluten.
(b) Dirt and dust.
(c) Grease and fatty matters.
(d) Metallic soaps.
(e) Coloring matters contained in the fiber.
(f) Resinous matters.

[2] The ink used for the marking of cotton cloth in bleaching may be made by dissolving tar in turpentine, or from a mixture of caoutchouc, benzine, and lampblack. This ink must be capable of resisting the boiling-out operations.

3. Singeing.

This process is for the purpose of removing the loose hairy fibers projecting from the surface of the cloth, and thus give it a smooth, even, and clean looking face. Generally, only one side of the fabric is singed, though in some cases both sides may require it. Calico which is afterwards to serve for print cloth is nearly always singed, otherwise the fine lines and traceries of a delicate pattern would be destroyed by the unevenness of the surface of the cloth. There are three methods by which singeing may be effected: (a) plate singeing; (b) roller singeing; (c) gas singeing. The method in plate singeing is to

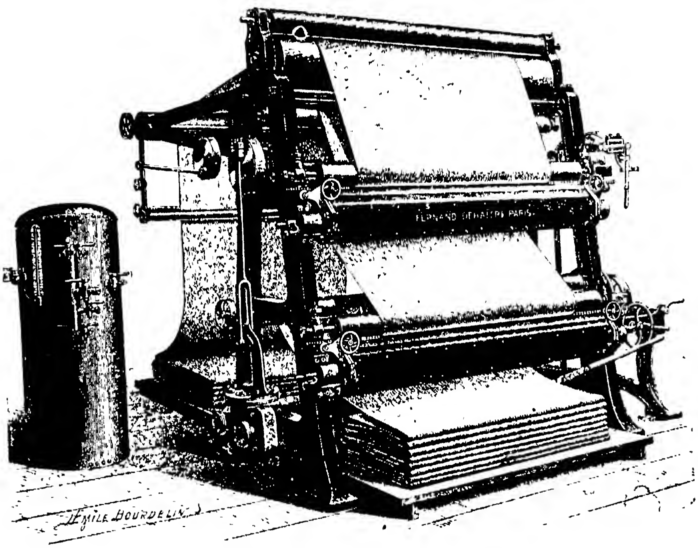


FIG. 215—Singeing Machine (French Type).

pass the cloth rapidly over a very hot plate, which will burn off the nap and yet not injure the general surface of the goods. The system is usually carried out by using two curved copper plates, arranged side by side, and heated either by a furnace or by a gas or oil flame. The cloth is drawn rapidly across these two red-hot plates, being held down against their heated surface by properly controlled rollers: Directly after leaving the plates the cloth is passed between two perforated steam pipes, or through a small trough of water, for the purpose of extinguishing any sparks which may still be adhering to the surface, as otherwise holes may be burnt in the fabric. The singeing plates are covered with a hood to carry off the sparks and products of the combustion. There is generally difficulty in obtaining even singeing by the use of red-hot plates, on account of not being able to

heat the plates with sufficient uniformity. By the use of a long burning gas or oil flame playing through the plates, more even results are obtained than when the plates are heated with a furnace.

Roller singeing is carried out in very similar manner to the foregoing, only instead of using stationary curved plates, the heated surface is a hollow revolving cylinder. The advantage of this over the previous method is that the singeing is more uniform, as it is possible to heat the cylinder more evenly than the plates, also the pieces can be singed twice on the same side in one operation.

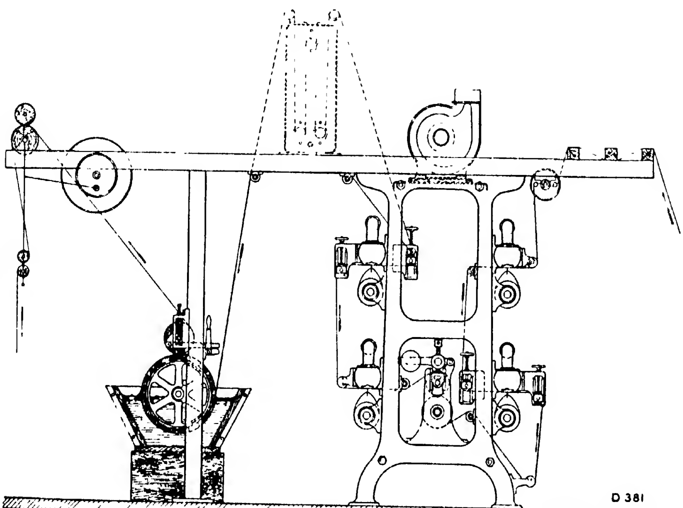


FIG 216—Diagram of Singeing Machine.

Gas singeing is carried out by rapidly passing the cloth through a Bunsen gas flame arranged in a long row across the width of the goods.[3] Sometimes several series of flames are employed, the cloth being passed over small rollers of copper containing water which prevents their becoming overheated; the use of the small rollers is to make the nap of the cloth stand out as much as possible so that it may be the more readily burnt off.

Plate or cylinder singeing is better adapted for thick and heavy cloth, whereas gas singeing is preferred for light and thin cloths. It is also more convenient to operate and control.

An objection to the plate method of singeing is that there is danger that the plates are not maintained at a uniform temperature, in consequence of which the cloth may be unevenly singed. It is claimed that gas singeing gives more even results, and especially with corded or

[3] The use of gas flames for singeing cotton cloth was introduced by Hall of Nottingham, about the year 1850.

that the steeping may be dispensed with without altering an any way the character of the bleach.[4]

In recent years malt preparations have been extensively used in the steeping process as these quickly solubilize the starchy matters present in the size and also the natural gums of the fiber.

In some establishments it is the custom to add a little soda ash to the steeping water (about 1 lb. of soda ash to 100 lbs. of cotton cloth). Spent lye liquors may also be employed for steeping, but they do not

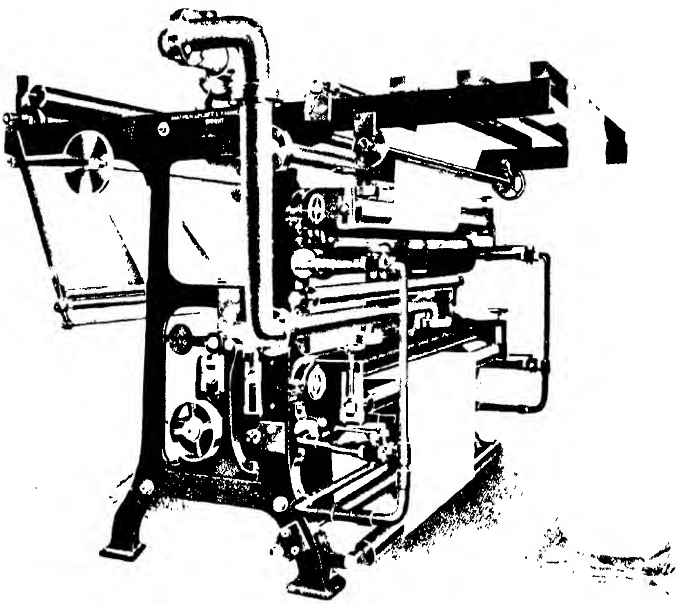


FIG. 220.—Two Burner Gas Singeing Machine (English Type).

appear to possess any advantage over hot water alone. After steeping, the goods are usually run in the chain form, and are conducted continuously through the succeeding operations from one process to the other, guided by means of porcelain pot-eyes. If the goods have been steeped in hot water, they should be washed afterwards in order to remove the soluble starchy matters.

5. Washing in Cloth Bleaching.

As nearly all of the bleaching operations are followed by more or less thorough washings, it will be well at this point to consider the process of washing in itself, and the remarks here made will suffice

[4] For fuller discussion of the subject of steeping as a process in bleaching and the use of malt preparations for this purpose, see page 225.

for all succeeding operations of washing. In the proper washing of the goods lies, to a great extent at least, the success in bleaching; and many faults are liable to arise from insufficient or improper washing. The washing after steeping is for the purpose of completely removing the fermented starchy matters which are quite soluble at this point; if the washing is incomplete, however, these substances on coming in contact with the alkaline liquors to which the cloth is next subjected may be so changed as to become insoluble again and offer considerable difficulty in the way of removal. After boiling in alkali, the washing accomplishes a double purpose; in the first place, the boiling lye changes the resinous and waxy matters of the cotton into soluble substances, of which, however, only a portion are removed by the alkaline liquors themselves; the remainder must be removed by proper washing, especially as the internal parts of the fiber are saturated with these substances, and if allowed to come in contact with the bleaching and acid solutions which follow the boiling in alkali, these matters will be deposited within the fiber as insoluble bodies, and the bleaching will be imperfect. The excess of alkaline liquor is also removed by the washing, and it is important that none of the alkali be left in the goods, especially if they are afterwards much exposed to the air, as under these conditions, oxycellulose will be formed, thus damaging and staining the fabric. Hence, the washing operation should follow reasonably soon after the treatment with alkali, and this is also the case for any of the other processes, and especially the goods should not be allowed to dry, even in places, before washing, as this will nearly always result in imperfections.

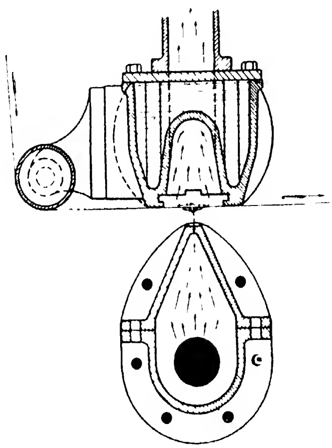


FIG. 221.—Section of Exhaust Chamber and Burner.

After treatment with the chloride of lime and acid solutions, the washing is chiefly for the purpose of removing excess of chemicals

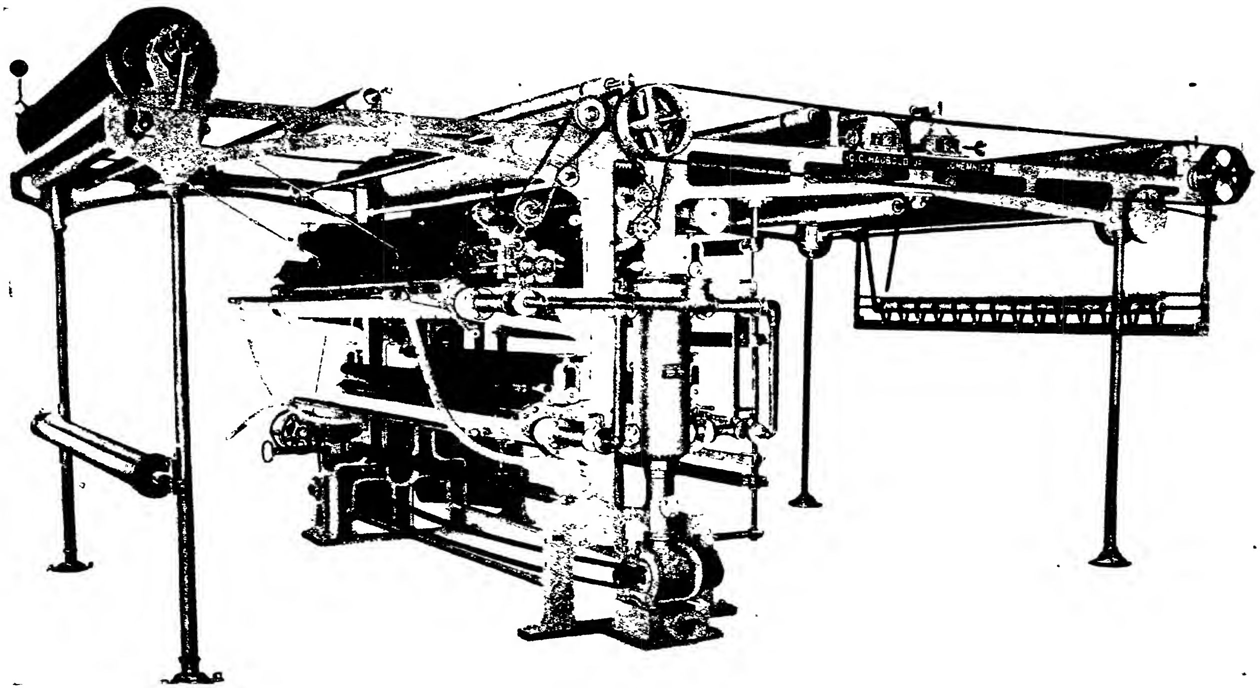


FIG. 222.—Gas Singeing Machine with Four Burners (German Type).

from the cotton, the retention of which would lead to damage of the goods, as the fiber saturated with such chemicals on exposure to the air is rapidly tendered. Also the washing prevents the too violent reaction which might take place between two chemicals on coming in contact with each other within the fiber, a condition which would surely be harmful. After boiling in lime, for instance, the goods are treated with an acid bath, for the purpose of removing the excess of lime; if the goods are not washed before being placed in the acid bath there will be a considerable quantity of lime which combines very vigorously with the acid, and the reaction may be sufficiently violent to do injury to the cotton in places. Washing after the bath of chloride

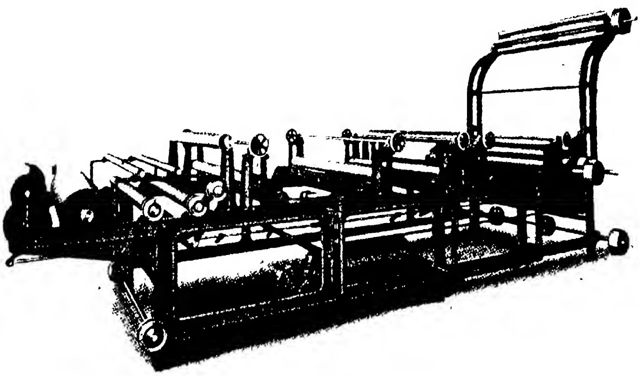


FIG. 223.—Five Burner Singeing Machine; Tulpin Style (Butterworth).

of lime is also very essential, for if the fiber still impregnated with bleaching powder solution is brought in contact with acid, a considerable quantity of chlorine will be liberated within the fiber and produce bad places in the goods. Finally, after acid treatments, a washing is always indispensable, for if any acid is allowed to remain in the goods, on drying or even on continued exposure to the air, a tendering of the fiber will rapidly take place.

The washing of goods may be carried out in three different ways: (a) in a wash wheel, (b) in a wash stocks or mill, and (c) in a roller machine for either rope form or open width. The last method is the one most usually practiced at the present time, although the other methods may have certain features which recommend them for use in special cases.

(a) The wash wheel consists of a large perforated drum set up on a horizontal axis, and revolving slightly submerged in a tank of water. The drum is divided internally into four compartments, each with an opening for the introduction of the cloth to be washed. The water is introduced through the hollow axis, which is perforated for this purpose. The impregnation of the cloth is assisted by the goods falling about as the drum rotates. For a wheel of about 6½ feet in diameter,

the speed should be 20 to 22 turns per minute, and the flow of water about 50 gallons per minute. Such a machine would carry about 25 lbs. of cloth in each compartment, or 100 lbs. altogether. Wheel washing is not used so much as roller washing, but in some instances it is employed for very fine fabrics, as by this method there is not as much wear on the goods as when washed in the roller machine, and also there is less opportunity of the goods becoming damaged.[5] It is also extensively used for washing small pieces, such as handkerchiefs, embroidery, ribbons, etc., which cannot be manipulated very well in the roller machine. Washing with the wheel is more expensive than roller washing, as it requires more labor and more time. The time required for washing in the wheel varies with the operation just preceding the washing, but the following is given by Tailfer as a working standard:

Previous operation	Time for washing, Minutes
Steeping	10
Lime boiling	15 to 20
Sour after lime	15 to 20
Lye boiling	12
Chloride of lime	12
Sour after chloride of lime	15
Last washing before finishing	20

The second method of washing is by means of stocks. This consists of a shallow bowl in which works a wooden hammer or plunger. The goods to be washed are placed in the bowl and are systematically squeezed and beaten by the moving plunger. In each drum or bowl there are usually two plungers working alternately. When the plunger is raised water enters the bowl and saturates the goods, and when the plunger falls the goods are compressed and the water is squeezed out and drains off. In an average machine the width of the bowl is about 4½ feet, and the width of the plunger about 2 feet; and the plungers strike about 30 blows per minute. Each bowl will hold about 150 lbs. of cloth, and the amount of water necessary is about 65 to 90 gallons per minute. According to the nature of the goods and the operation preceding the washing, the time for washing in the stocks will vary. Tailfer gives the following standards from practice:

Previous operation	Time for washing, Minutes
Steeping	30
Lime boiling	40
Sour after lime	35
Lye boil	30
Chloride of lime	30
Sour after chloride of lime	35
Last washing before finishing	45

Washing with stocks is an excellent method as the water is made to penetrate very thoroughly by the pounding of the hammers; it is not

[5] Wash wheels were once quite extensively used even for the washing of cloth, especially in England, but at the present time they are no longer used except for special purposes.

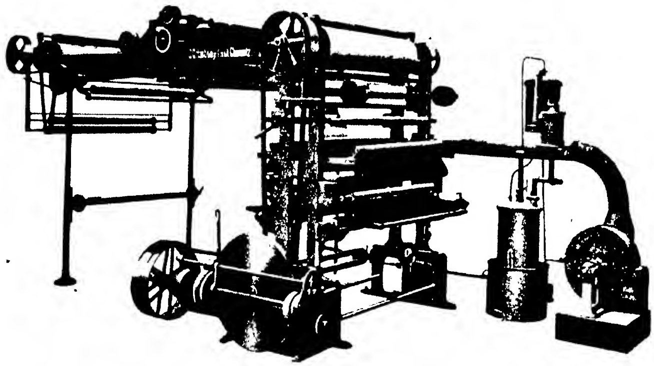


FIG. 224.—Gas Singeing Machine with Brush Rolls and Fitted for Benzol Gas Apparatus.

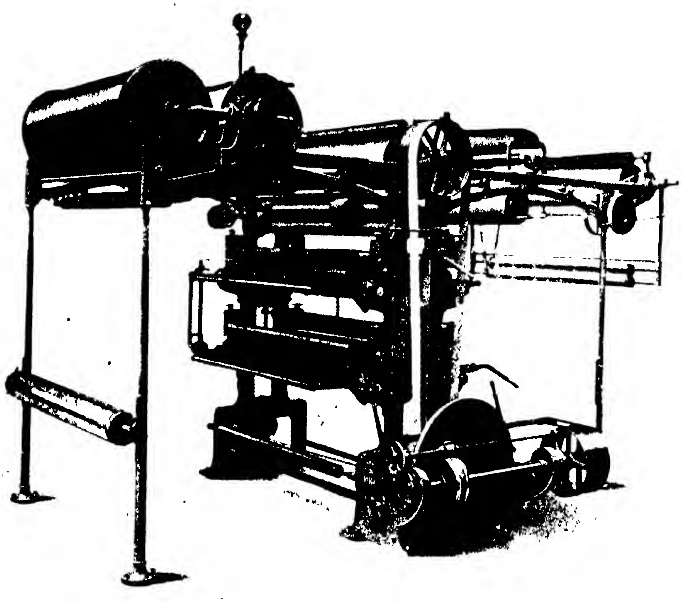


FIG. 225.—Singeing Machine with Drying Cylinders and Steaming Arrangement.

adapted, however, to heavy goods, and is mostly employed for washing small pieces. This method is much more costly than the roller process, and generally this consideration alone prohibits its use.

Another form of the stock or hammer washing machine is the so-called tom-tom which consists of a vat or container for the goods

which is made to automatically move backward and forward while the goods are being subjected to the action of falling hammer blows. The machine is also made in the form of rotating circular vat with alternating hammers rising and falling. This method of washing is still used to a considerable extent for lace goods and similar articles which cannot be satisfactorily washed in the roller washer. The pounding action of the tom-tom is not as severe as that of the stocks as the action is distributed more evenly over all parts of the material. The beaters or hammers are raised by means of suitable cams and are then allowed to fall of their own weight.

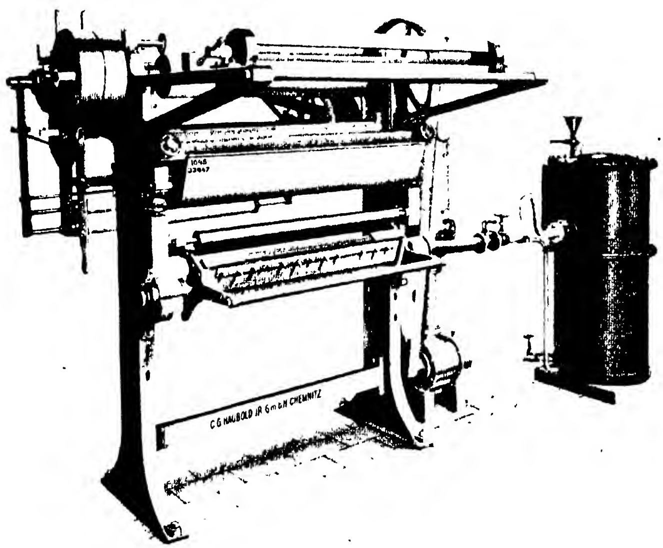


FIG. 226.—One Burner Singeing Machine with Gasoline Apparatus.

Very often, in order to economize both labor and time, the washing of the pieces is conducted in the same kiers as the steeping, boiling, etc.; the previous bath being run off and fresh water admitted and circulated through the goods in the same manner as the previous bath. This method, however, is seldom very satisfactory as the washing is by no means as thorough as it should be, and portions of the material will be incompletely washed, so that subsequently stains and uneven places are liable to form.

The roller washing machine consists essentially of two wooden cylinders turning on each other; the lower one being turned by power. The machine contains below a trough for water, the latter being introduced in the form of a spray or shower over the goods. The cloth in rope form is passed through the machine spirally so as to be carried through the water several times and is held in place by a sub-

merged roller underneath the water in the tank. On the upper roller of the machine at each end there are situated two short heavy rollers serving the purpose of squeezing the cloth as it enters and comes from the machine, the pressure on the two rollers being adjustable by means of sliding weights. In order to prevent the goods from sticking to the rollers and being drawn in and around with them, thus causing damage, the machine is provided in the forward part with a rotating reel, which revolves somewhat faster than the wash rollers, and thus is continually drawing the goods from the rollers. In some forms of washing ma-

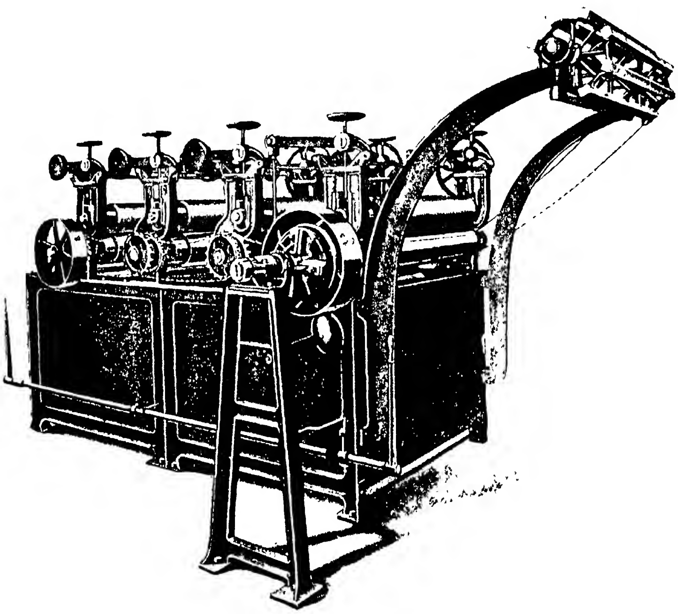


FIG. 227.—Open Washer for Piece Goods (Text. Fin. Mchy. Co.).

chines, two or more strands of cloth may be passed through at once, being guided in their course by means of wooden pegs. Washing machines may be either of the tension or non-tension varieties; in the former the goods are stretched by passing around a roller located at the bottom of the water tank, whereas in the non-tension machine several yards of the goods are left slack in the water. The tension machine is used for heavy goods which are stiff and will not sink in the water readily, and is also used when the goods are passed through the machine very rapidly to prevent them from becoming entangled. The non-tension machine is used with light souple goods that readily sink and also when washing at low speed. By leaving some of the cloth slack in the water it has more chance to work about and the water

penetrates much better. Tension machines must be used when the cloth is run at a velocity of 400 to 500 feet per minute, and non-tension machines when the velocity is only 200 to 300 feet per minute, although when very bulky pieces are being washed the speed may be reduced to 50 to 100 feet per minute. In order to increase the life of the wooden bowls and also to give them a better surface for drawing

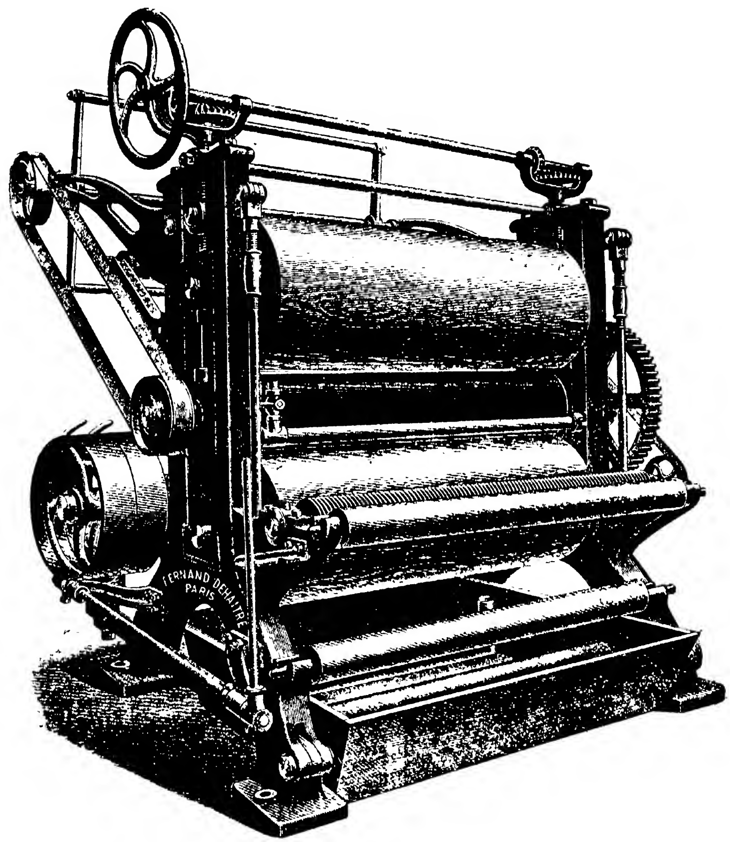


FIG. 228.—Water Mangle or Squeezer (French Type).

in the cloth, they are often covered with hemp rope. As the rope wears down it may be easily renewed and thus the diameter of the roller is kept constant. In most machines the lower or main roller is about two feet in diameter, and the upper one, which merely serves to press the goods on the lower roller, about one foot to eighteen inches in diameter. In order to prevent the rollers from wearing in grooves by

the cloth always passing over the same place, the ladder of wooden pegs which guides the pieces should be moved backwards or forwards from time to time, and thus change the position of the cloth. The best wood for making the wash rollers is beech, plane, or cypress, and the wood should be well seasoned and have been preserved for a long time under water.

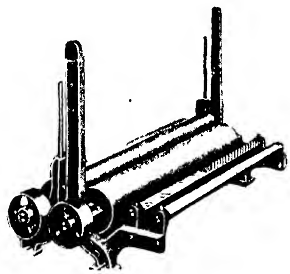


FIG. 229.—Rolling Machine for Bleached Cloth (Curtis & Marble).

The manner of introducing the water in washing is of importance, the best way being to have the exit pipe at the end where the goods enter and the water is introduced at the end where the goods leave, as in this manner the pieces will come in contact with pure water at the moment of exit. The rate of flow of water will naturally depend on the speed with which the goods are run through the machine, but in general it will require from 150 to 225 gallons per minute. The number of times the goods should circulate through the string tub washer should be at least 8 to 10, and hence the rollers should be 10 to 11 feet in length.

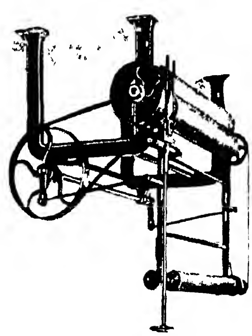


FIG. 230.—Overhead Folder (Curtis & Marble).

Besides the string tub machine for cloth in the rope form there is also used a washing machine for cloth in the open width. This machine usually consists of a series of several tanks with squeeze rolls

between and provided with submerged guide rolls. The cloth is led continuously through the machine and frequently there are provided specially constructed appliances to beat the cloth and whirl the water forcibly against it to bring about more rapid and thorough washing.

6. Composition of Effluent Wash-waters in Cloth Bleaching.

Naylor[6] gives the following analyses indicating the general nature of the various effluent liquors from the different operations in cloth bleaching, in works where the lime and soda ash process of boiling-out is practiced:

Volume Gallons	Wash-water	Dissolved Solids			Suspended Solids			Total Solids	Acidity Normal NaOH required	Alkalinity Normal H_2SO_4 required
		Mineral	Volatile	Total	Mineral	Organic	Total			
		Parts per 100,000							Parts per 100	
	Water supply from reservoir	8.0	10.3	18.3	..	....	....	18.3		Neutral
20,000	First wash, or steep	42.9	145.1	188.0	16.4	55.9	72.3	260.3	0.2	..
1,600	Waste lime liquor	134.3	613.8	748.1	9.0	105.0	114.0	862.1	....	1.4
20,000	Wash from lime kier..	22.8	25.7	48.5	6.8	9.7	16.5	65.0	....	0.3
1,600	First (gray) sour........ .	288.9	131.4	420.3	8.8	55.9	64.7	485.0	32.7	..
10,000	Wash from gray sour.. . .	42.7	22.0	64.7	3.4	10.7	14.1	78.8	1.5	..
1,400	Waste soda ash liquor ...	802.1	556.4	1358.5	included with dissolved solids			1358.8	....	10.1
20,000	Wash from soda ash.......	30.7	20.2	50.9	3.0	9.0	12.0	62.9	....	2.0
1,600	Waste chemic	114.3	29.8	144.1	8.6	11.5	20.1	164.2	....	0.3
1,600	Second (white) sour	126.5	47.5	174.0	1.2	7.1	8.3	182.3	10.9	..
20,000	Final wash	8.2	12.1	20.3	2.9	11.2	14.1	34.4	0.3	..

7. Hydro-extraction.

Frequently after washing, the goods are squeezed or hydro-extracted in order to remove the surplus water from the fiber, the retention of which would otherwise dilute too much the action of the chemicals of the succeeding bath. If this water is not removed after washing, the strength of the next bath, whether alkali, hypochlorite or acid, must be increased in order to obtain the proper results, and in this way the cost of the operation would be increased perhaps far beyond the added expense of squeezing. Sometimes the washing machine itself is provided with an attachment for squeezing the cloth as it passes out; at other times a special squeezing machine or water mangle is used. This merely consists of weighted squeeze rollers playing on a hard rubber roller under pressure. Another method is to use a centrifugal machine or hydro-extractor, or as it is frequently called, a "whizzer." This consists of a perforated cage mounted on a vertical shaft which is rotated very rapidly. The goods are placed in the cage and the excess of water is thrown off by means of the centrifugal action of rapid rotation. The motion may be communicated to the shaft by means of friction cones or other suitable arrangements; in some cases the shaft is driven directly by means of a small attached engine. The use of hydro-extractors does not cause any wear or in-

[6] *Jour. Soc. Dyers & Col.*, 1896, p. 98.

jury to the goods, and they also remove the water very thoroughly. They require, however, the expenditure of considerable power and labor, and do not carry very large amounts at a charge, consequently this method is much more expensive than that of merely using squeeze rollers.

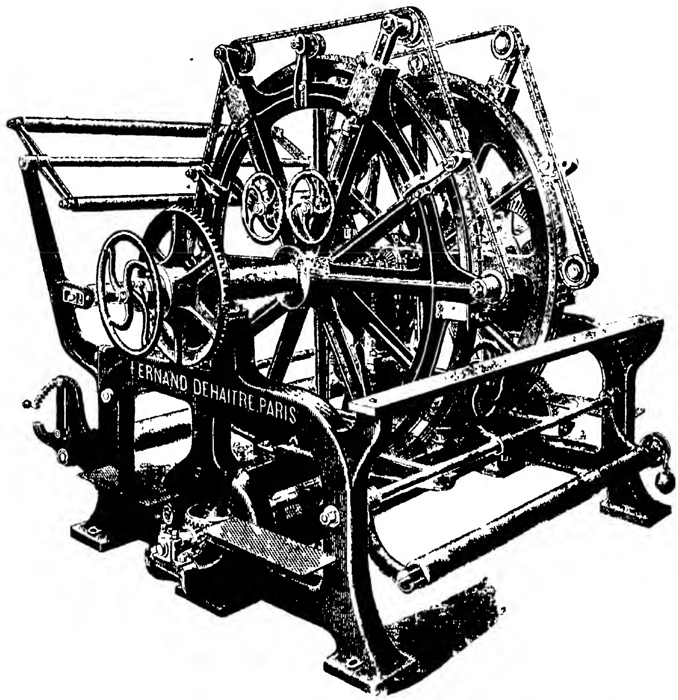


FIG. 231.—Revolving Expander for Bleached Cloth (French Type).

There is also a form of centrifugal hydro-extractor used for cloth in the open width and wound on a cylinder which is made to rotate very rapidly. There is also another machine for open-width goods where the pieces are passed over suction pipes connected with a vacuum pump. Neither of these machines, however, is much used for cotton goods.

8. **Bleaching with the Mather-Platt Kier.**

In this system a specially constructed kier is used together with a modified method of bleaching originated by Koechlin. In the boiling-out process, the lime and soda ash boils are dispensed with and replaced by a single lye boil with caustic soda and resin soap, and in some cases even the latter is omitted. The kier consists of a large cylinder

of wrought iron and placed horizontally; one end is provided with a door capable of being screwed down steam-tight. The goods are

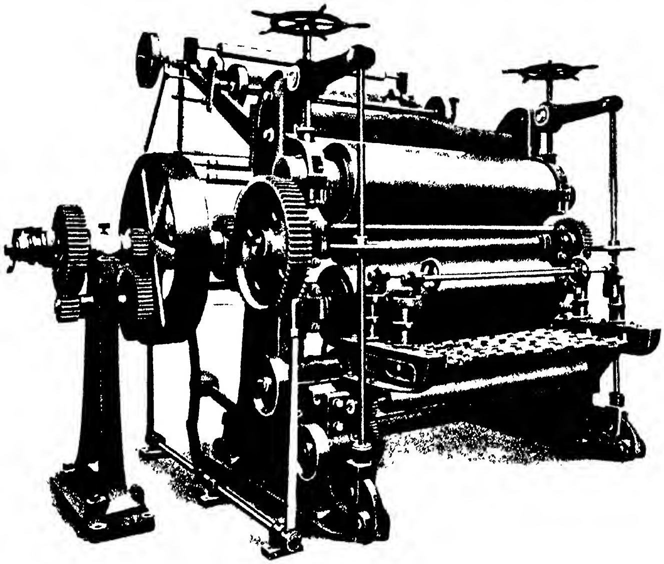


FIG. 232 – Friction Calender for Bleached Goods.

packed into iron wagons provided with false bottoms, and usually of such a size that the kier will hold two wagons. These wagons are

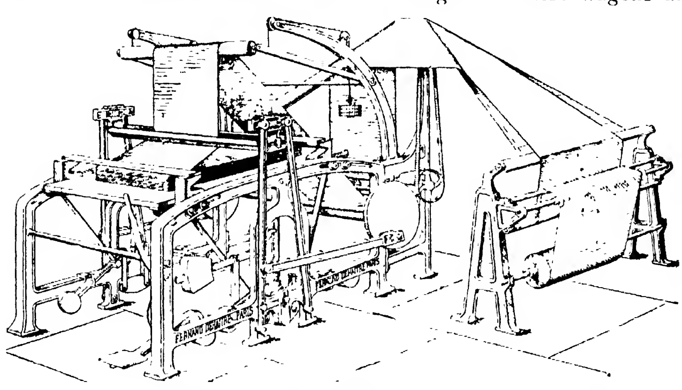


FIG. 233.—Doubling and Folding Machine for Bleached Goods.

run into the kier on rails, after which the door of the kier is closed and the air is driven out by the admission of steam. The caustic

liquor is then pumped into the kier and spread over the goods in the wagons by means of a spray. After passing through the goods the liquor collects in the false bottom of the wagon and is pumped back over the goods again. The caustic liquor is heated by means of a

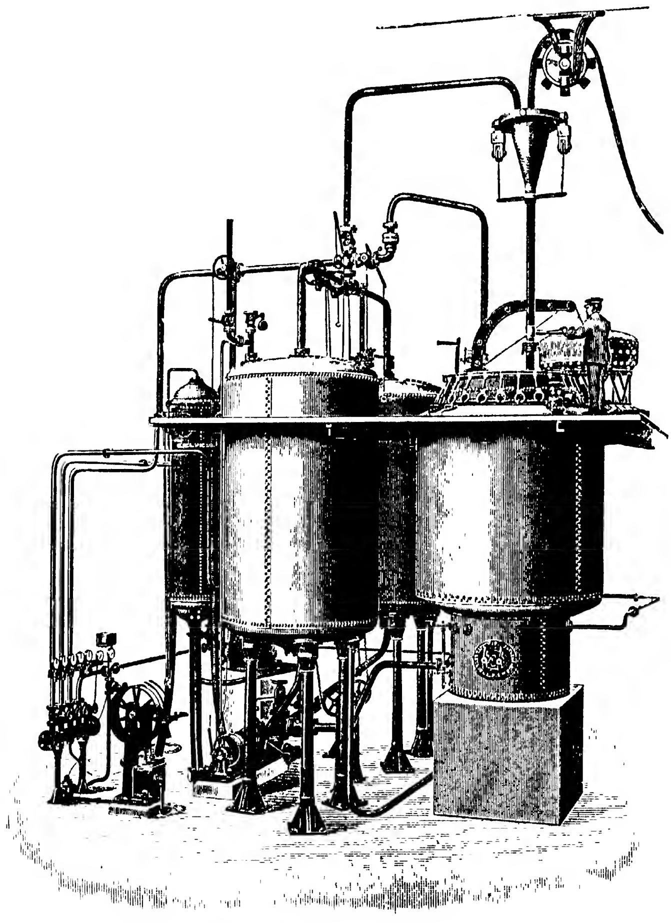


FIG. 234.—Thies Bleaching Installation for Cloth.

steam coil at the bottom of the kier, or it may also be heated by direct steam from a perforated coil. In order to prevent the dilution of the lye by the condensed steam on the inside of the kier, it is so arranged that the water thus condensed runs down the sides of the kier into an outlet pipe which does not communicate with the lye. The amount of

lye required for this kier is about 20 gallons per 100 lbs. of goods. Usually the kier is run for an hour at a boil under ordinary atmospheric pressure, then the pressure is raised and the boiling continued for 6 to 8 hours. The steam is then shut off, the caustic liquor removed, and the goods are washed in the kier by circulating water in

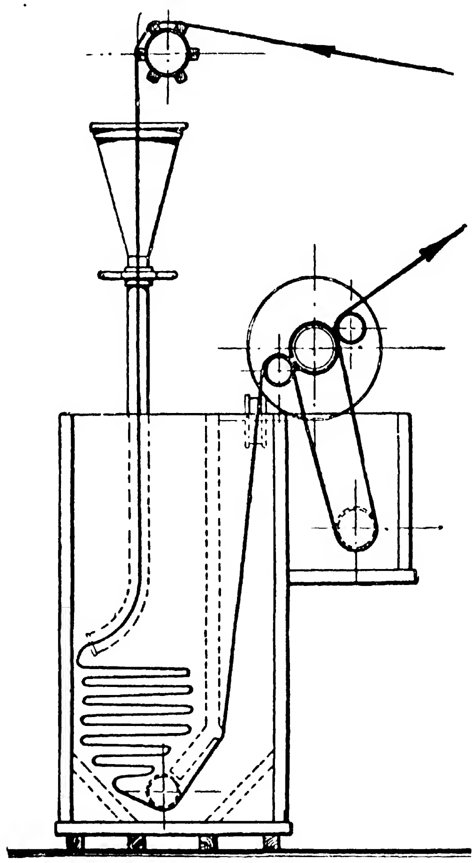


FIG. 235.—Continuous Chemicking and Souring Apparatus for Thies System.

the same manner as the lye. First a wash is given with about 25 gallons of water per 100 lbs. of goods; after this has circulated for ½ hour it is run off, another 25 gallons of water per 100 lbs. of goods are run in, and the washing repeated. The wash waters are heated in the kier by steam. After the washing is finished, the door of the kier is opened and the wagons are run out, and the goods are then passed

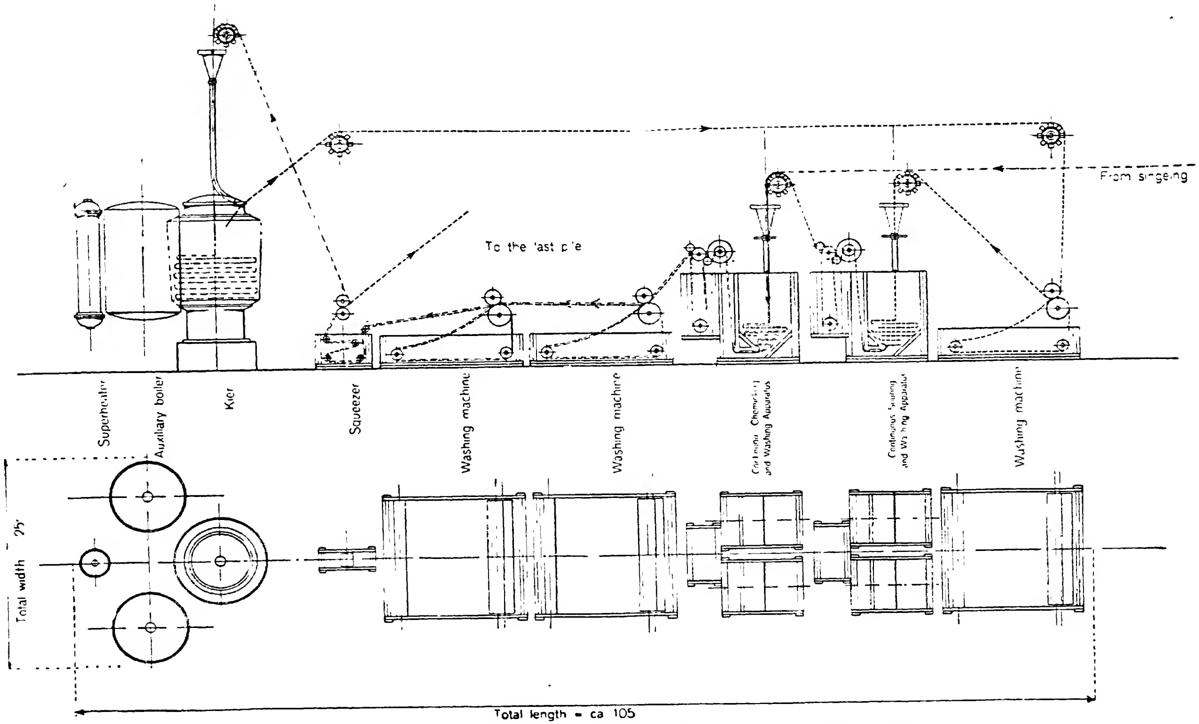


FIG. 236.—Complete Layout for Thies System of Bleaching Cloth.

through the treatments with chloride of lime, acid, etc., as usual. The advantage of using the Mather kier is that the fabrics may be boiled-out rapidly by the use of caustic soda without risk of injury. Caustic soda has a much more energetic action than soda ash or lime, and a better white is obtained in a fewer number of operations. The ordinary kier cannot be employed for this method of boiling as caustic soda in the presence of air will rapidly cause injury to the cotton; but in the Mather kier the air is all expelled by means of steam before the caustic liquor is run in. It is also a good precaution to saturate the goods with caustic soda before entering the kier, so that less air will be introduced. There is also a considerable saving in water, time, labor, and power in the operation of this kier.

Koechlin gives the following details for the working of this process in connection with the kier: The pieces in the gray are passed through sulfuric acid at 2° Tw., and left in the acid for 10 hours, after which they are washed and passed at 170° F. through a solution containing 450 gallons water, 55 lbs. caustic soda, and 1¼ gallons sodium bisulfite (64° Tw.) for every 250 pieces of 100 yards each. The goods are then packed evenly into the wagons and run into the kier, where they are treated for 8 hours under 7 to 15 lbs. pressure with a solution containing 500 gallons water, 66 lbs. caustic soda, 88 lbs. soda ash, and 44 lbs. rosin. Then the goods are washed in the kier several times with water.

Mather and Platt have recently devised a system of bleaching in the open width, or rather in rolls. The cloth is saturated with a solution of alkali and wound on a specially constructed roller provided with a perforated end plate and suction chamber; the roll is then run into a special form of kier which, it will be seen, is of the horizontal type with a valve door capable of being made steam tight and working under 40 lbs. pressure. After the carrier containing the roll of cloth is run into the kier the door is closed, and the boiling-off or alkaline liquor is circulated through the goods by means of a centrifugal pump; the principle of the circulation being that the liquor is drawn from the suction chamber behind the perforated plate at the end of the roll, the whole of the cloth being submerged in the liquor while the roll with perforated plate is slowly revolved during the boiling; thus a thorough circulation of the liquor takes place longitudinally between the folds of the cloth on the roll from selvage to selvage. After the boiling-out with alkali is finished, the liquor is drawn off and water is admitted and circulated in the same manner. The goods are then removed from the kier and placed in a chemic tank, so connected with the roll and its perforated plate that the bleaching liquor is circulated in the same manner as the liquors in the kier. The fittings of this open bleaching bath are of such a character as not to be acted upon by acids, alkalies, etc. After the chemicking or chloring operation is completed, the rinsing, souring, and washing operations are carried out in the same bath without removing the roll of goods. After the bleaching operations are through, the roll is removed and the cloth is wound off, passed through squeeze rolls, and finally over drying cylinders.

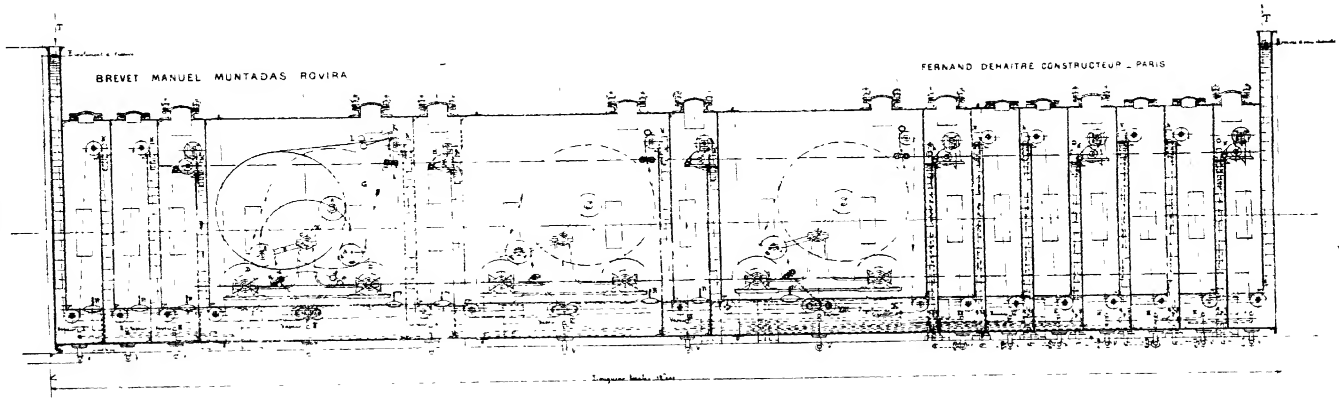


FIG. 237.—Muntadas Kier System of Bleaching.

9. Other Methods in Bleaching Cotton Cloth.

In order to lessen the time required for bleaching and also to lower the cost due to labor, various methods of continuous bleaching have been suggested.[7] The Mather-Thompson continuous bleaching apparatus consists of a long kier composed of 15 partitioned compartments, and is built for use of goods which have been boiled out in the Mather kier. In the first compartment the goods are run through hot water; in the second through chloride of lime at 2° Tw.; in the third through carbonic acid gas; in the fourth, fifth, and sixth through cold water for washing; in the seventh through a solution of soda ash at 75° F., and containing about 1 lb. per 100 gallons; in the eighth, ninth, and tenth the goods are washed again with water; in the eleventh through chloride of lime at ½° Tw.; the twelfth, through carbonic acid gas again; the thirteenth, fourteenth, and fifteenth through 1 percent solutions of hydrochloric acid. On leaving the machine the goods are washed as ordinarily, and dried. The use of the carbonic acid gas is to cause the chloride of lime to act more rapidly on the coloring matters, through the liberation of free hypochlorous acid in the fiber. Instead of carbonic acid gas, weak solutions of acetic acid may be used to effect the same results.

The Thies system of bleaching cloth has been received with considerable favor in Germany. It is a continuous process and is said to have the advantage of greatly reducing the labor required. The general scheme of the process is illustrated in Figure 236, showing the elevation and floor plan of the various machines. After singeing the goods are first soured and then washed in a continuous apparatus. They are then boiled in the kier and then taken through a second continuous washing, chemicking and souring to the final stage of finished goods. The chemicking and souring machine is shown in Figure 235, together with the mechanical plaiter in the form of an elephant's trunk. The special kier used in this process has already been described in preceding pages. The washing apparatus is shown in Figure 236, and is also of special design. The boiling-out is conducted at high pressure (45 lbs.) and with concentrated alkaline liquor (caustic soda solution of 6-7½° Tw.).

[7] Professor Koechlin has introduced the following method of bleaching, by which it is claimed that a better white can be obtained than with chloride of lime and with less damage to the fiber. The cotton is passed through a bath of 100 liters of water, 10 kilos. of lime, and 50 kilos. of sodium bisulfite. The material thus impregnated is then steamed for one to two hours under a pressure of from one to two atmospheres. Instead of steaming, the cotton may be boiled in the bath for several hours. The exact *rationale* of this method is not clearly understood, and the author has not been able to discover that it has been used to any extent in practice.

Chapter XXII.

The Bleaching of Special Cotton Fabrics.

1. Bleaching of Knit-goods and Hosiery.

White cotton knit-goods (hosiery, underwear, etc.) may be knit from bleached yarn or from gray yarn and then bleached in the piece. In the former case the bleaching of the cotton is carried out in the same manner as for any purpose of yarn-bleaching, care being taken to keep the fiber in as soft and lofty a condition as possible.[1] There is only a comparatively small proportion of hosiery bleached, as this article is most largely marketed in the dyed condition. Underwear, however, is very largely bleached at the present time, and this is especially true of knitted underwear fabrics of the medium and lower grades which are made from carded cotton yarns. These yarns contain quantities of motes and are in general of a dirtier character than the higher-grade combed yarns, consequently in order to obtain a knitted fabric of pleasing appearance it is necessary to resort to bleaching. In a great deal of knitted underwear from combed yarn a bleached yarn itself is used, but in fabrics made from carded yarns it is very seldom that bleached yarns are employed, and consequently the bleaching is done in the knitted piece. Bleaching in the piece is also more and more being resorted to in the case of combed yarns, as it is not only cheaper, but also due to the fact that there is always more or less staining and dirt accumulation in the knitted fabric in the various manufacturing operations through which the material has to pass, a yarn-bleached fabric is not as clean as one bleached in the piece after manufacturing. On the other hand, there are certain disadvantages of bleaching in the piece. When the fabric is knit from a previously bleached yarn and not processed to any extent after manufacture, the structure of the fabric will retain more perfectly its arrangement and alignment, whereas when the manufactured fabric itself is bleached, it passes through a variety of operations in which it is subjected to considerable tension and strain, consequently the structure of the fabric is more or less distorted and this has to be corrected by proper stretching in drying, and this, of course, reduces the elasticity of the garment.

There are two general methods of bleaching knit-goods, the first

[1] In the consideration of the bleaching of different varieties of special fabrics it is difficult to avoid a certain amount of repetition in the description of the processes and at the same time preserve the proper unity and order in the sequence of the operations. The details and principles underlying the operations have been fully discussed in the preceding chapters, and therefore in the description of these particular phases of the subject only the more general outlines are given. Even under these circumstances, however, a certain amount of repetition has been unavoidable, though its necessity will be appreciated by the critical reader in the proper presentation of the subject.

with peroxides and the second with hypochlorites. The former process is generally used on high-grade fabrics where the relatively higher cost is warranted, whereas bleaching with hypochlorites is generally practiced on medium and low-grade fabrics and more especially on those made from carded yarns. In this case, the chief function of the bleaching process is to destroy and remove the motes, and this can

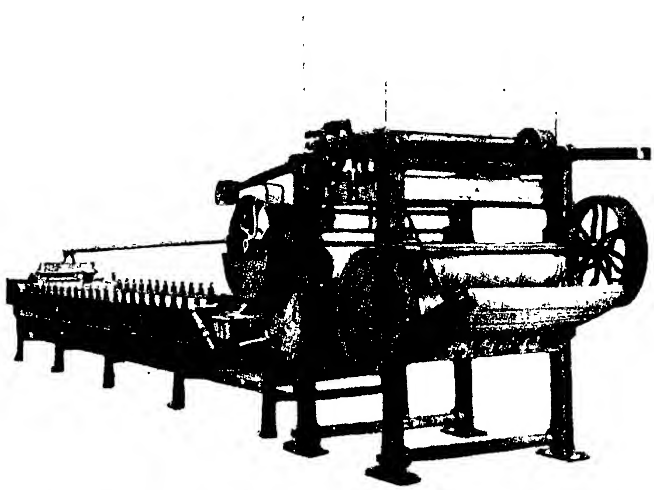


FIG. 238.—Continuous Washing and Scouring Machine for Hosiery (Pegg).

only be successfully accomplished by thorough boiling-out and then bleaching with hypochlorites. The peroxide method yields a product which is softer and more lofty in character and preserves much better the elasticity of the fabric; also in the case of luster-yarns, such as mercerized cotton, the high finish of the fiber is better preserved. The hypochlorite method, on the other hand, is considerably cheaper and also gives a whiter bleach.

2. Peroxide Method of Bleaching Knit-goods.

When bleaching with the peroxide method, the preliminary boiling-out of the cloth is usually done with a soap solution or with a solution of soluble oil, such as Turkey-red oil, Monopole Oil, etc., the operation being conducted in an open string-tub machine. A solution containing from 2 to 5 percent of soap on the weight of the goods is used, and the cloth is run in this bath for one hour at a temperature of 180° to 200° F. The goods are then thoroughly washed with hot water which should be as soft as possible. If hard water is used, the soap residues are liable to be precipitated in the cloth and streaks and stains may be developed in the bleached goods. The bleaching with

peroxide is conducted by the use of either hydrogen peroxide or sodium peroxide. Generally a ½ percent solution of peroxide is employed, though in some cases as high as a 1 percent solution is used. For the preparation of a ½ percent solution, 1 gallon of hydrogen peroxide liquor (as purchased in carboys and containing 3 percent of active peroxide) is used for each 5 gallons of water in the bleaching bath; for a 1 percent solution, of course, just twice the quantity of hydrogen peroxide is added. Also sufficient ammonia or sodium

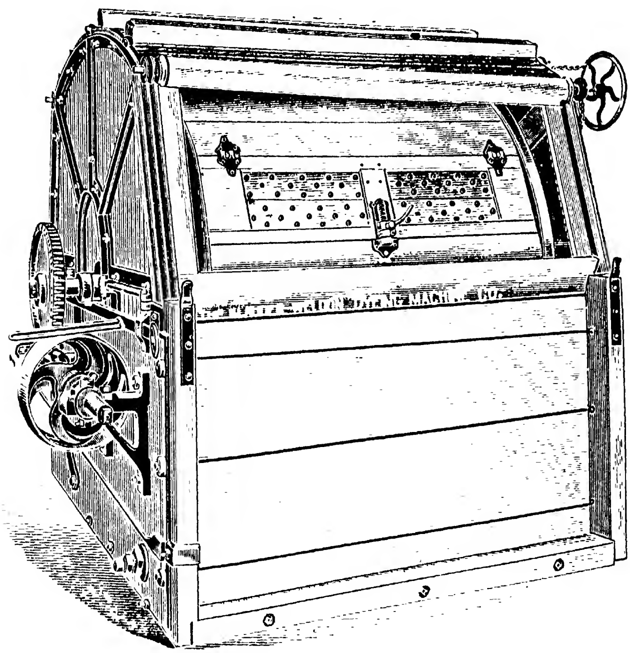


FIG. 239.—Wooden Machine for Washing and Bleaching Hosiery.

silicate is added to the bleaching bath to give a decided alkaline reaction. The bleaching operation may be conveniently carried out in a lead-lined roller washing machine, the cloth being run in a continuous rope form for an hour at a temperature of 160° F., and then sunk down beneath the liquor for 6 to 8 hours, keeping the temperature at about 120° to 140° F. Frequently the bleach is completed by running the goods for an hour at nearly a boiling temperature. The cloth is then removed and run through a washer and thoroughly rinsed with warm water. Often a clearer white can be obtained by adding a small quantity of oxalic acid to the wash water. When sodium peroxide is

employed, the bleaching bath is prepared in the usual manner as described on page 370.

3. The Hypochlorite Method for Bleaching Knit-goods.

In the hypochlorite bleaching process, there are two main points to be considered—firstly, the boiling-out with alkali; and secondly, the bleaching proper with chemic, which may take the form of a number of different hypochlorite solutions. A long experience has shown that by far the principal factor in the successful bleaching of knitted fabrics made of low-grade carded yarns is a thorough and well-understood boiling-out. If the boiling-out operation is incomplete or improper, the motes cannot be satisfactorily removed, even though the subsequent treatment with chemic be sufficient to produce a good white color in the fiber. Furthermore, the less perfect the boiling-out, the more violent will have to be the action of the chemic; stronger solutions of both chemic and acid will have to be used, with a consequent danger of tendering the goods and making them harsh and stiff. Besides this, the cost of the bleaching will be much higher than when a better boiling-out is given.

4. Boiling-out of Knit-goods.

There are a number of methods of boiling-out in vogue for knit-goods, the particular method used being more or less dependent on the conditions in the case, and the experience and personal caprice of the bleacher in charge. The older process of boiling-out, and one which is still largely in use, employs open wooden kiers. The goods are folded down in a continuous chain in these kiers, which are merely large round wooden tubs provided with a perforated false bottom, and a slatted wooden top to hold the cloth in position during boiling. The liquor is circulated by the force of steam injectors in one or several pipes placed on the outside of the kier and connected with the well at the bottom of the kier beneath the false bottom.[2] The liquor employed for boiling-out consists for the most part of a solution of caustic soda, from 3 to 6 percent of the alkali on the weight of the goods being employed. In connection with the caustic soda there may also be used silicate of soda (from 1 to 4 percent), soda ash (from 1 to 3 percent), and sometimes soap and Turkey-red oil (soluble oil) are also used. Sometimes proprietary "bleaching assistants" are used in connection with the caustic soda. These compounds are mostly composed of an intimate mixture of caustic soda, soda ash, and silicate of soda finely ground together and sold to the bleacher at a high price. In some cases they are quite efficacious, but their cost is high, and the bleacher could make up the same mixture himself at a much lower cost. In other cases, these "bleach assistants" are distinct frauds, being composed of caustic soda ground up with common salt and glauber-salt, with more or less soda ash, and their boiling-out value is really considerably less than ordinary caustic soda and soda ash.

In the open-kier method of boiling-out it requires from 10 to 12

[2] See page 279 for detailed description of kiers.

hours (usually overnight) to obtain a satisfactory treatment of the goods, and this long time in contact with the hot alkali has a tendency to make the cloth harsh, and also to decompose the cotton-wax on the fiber into resinous bodies which may discolor the goods and which are difficult to wash out. The use of soap and soluble oil will lessen these defects and leave the goods whiter and softer after the boil. The open-kier method also requires a relatively large quantity of chemicals, and a high consumption and waste of steam. Owing to these disad-

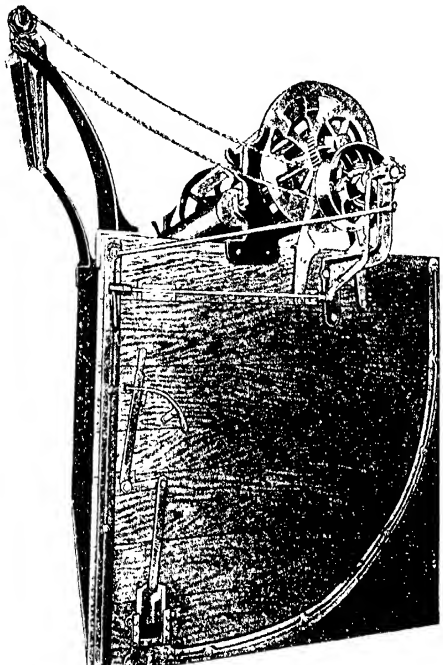


FIG. 240.—Roll Machine for Bleaching Knit-goods (Kaluder-Weldon).

vantages many bleachers of knit-goods have introduced closed kiers working under pressure (usually from 10 to 12 lb. steam pressure). Such kiers are constructed of iron, and the circulation is produced in a variety of ways. In some, a central inside vomit pipe runs from the bottom well of the kier, and the liquor is forced up this pipe by a steam injector, and is sprayed over the top of the goods. In other kiers, the circulation pipes are on the outside and the liquor is forced around by a special form of steam injector valve. In another variety (quite popular in England) the circulation is produced by a pump, and the liquor is forced through an outside chamber containing a heating

coil. A later form of kier, and one which is becoming very popular on account of its novel and economical method of operation, circulates the liquor by means of a vacuum chest.[3] In this chest there is first admitted high-pressure steam which operates an automatic cut-off valve when a certain pressure is reached. At this point connection is made with the liquor at the bottom of the kier, which, coming in contact with the high-pressure steam, immediately condenses it, thus producing a vacuum which draws up the liquor from the kier until the chest is full. This causes an automatic shut-off of the connection with the kier-liquor, and opens up the valve admitting the high-pressure steam; and the latter both heats up the liquor and forces it over to the top of the goods within the kier. A continuous cycle is thus obtained working under automatic conditions.[4]

After the boiling-out operation has been completed it is essential that the knit-goods be given a thorough washing with water in order to remove the soluble and decomposed matters resulting from the action of the chemicals on the impurities in the fiber. These matters are brown in color and mucilaginous in character, and unless thoroughly removed from the cotton immediately after boiling-out and before they have had a chance to become dry, may lead to the formation of brown stains. This washing operation is usually conducted in the kier after the boiling-off liquors have been run off.[5] A further washing is usually given after the goods have been taken from the kier and before they are treated with the chemic solutions for the bleaching proper.[6]

5. Hypochlorite Treatment for Knit-goods.

There are several methods in vogue for conducting the treatment with chemic. The older method, which is still largely employed, may be called the "continuous process." In this method the cloth is run out from the kier over a roller and through pot-eyes, and is carried into a tank containing the chemic solution, consisting of chloride of lime or

[3] Jefferson-Walker kier, see page 237 for detailed description. The automatic circulation of this kier is now rendered more positive by the use of an electrically operated valve.

[4] The amount of chemicals used for boiling-out knit-goods in this kier is comparatively small, 2 percent of caustic soda, 1 percent of soap, and ½ percent of soluble oil (on the weight of the goods) being a good proportion.

[5] The wash-water employed for this purpose in the kier should be hot, and not cold. If cold water is used there will be danger of precipitating more or less the impurities which have been dissolved from the cotton, though not yet removed from the kier. The impurities existing in the cotton fiber consist mostly of so-called pectin matters. By the action of the alkali and oil which are used in the kier for boiling-out, an emulsification takes place. The resulting product is a brown, rather slimy mass, which, though soluble in warm water, is not very soluble in cold water. Consequently, if cold water is run into the kier directly after the boiling-out has taken place, there will be considerable danger of a precipitation within the folds of the goods of this brown pectin matter, and this may be rather difficult subsequently to get rid of, and may give rise to stains, and very likely manifest its presence throughout the entire bleaching operation. On this account it is strongly recommended to use hot water, especially in the first wash-off after the boiling-out has been given in the kier, and before the goods are removed from the kier. This wash-water should be circulated through the goods for about 15 to 20 minutes.

[6] It often happens that the water employed for washing contains some dirt or iron compounds, and as the cloth acts as a filter in the kier, stains may develop on the goods which are subsequently very difficult to remove in the bleaching process. In such cases the goods should be well washed after being taken from the kier, and a small quantity of muriatic or sulfuric acid should be added to the wash water (about 1 ounce of acid to 10 gallons of water will usually be sufficient). It must be borne in mind, however, that after such an acid treatment, the goods should not be allowed to stand around and dry-out in spots, as otherwise tender places are liable to develop. There is no danger, however, if the goods are run from the acid bath immediately into the chemic bath.

sodium hypochlorite at 2° to 3° Tw. The goods pass under a roller at the bottom of the tank so as to keep them submerged beneath the liquor during their passage. The cloth then passes out of the chemic tank through large squeeze rolls, so that the excess of the liquor returns to the chemic tank. The goods, however, must not be squeezed with too great a pressure, as it is necessary to leave sufficient liquor in the cloth to do the bleaching. The cloth, now saturated with the chemic

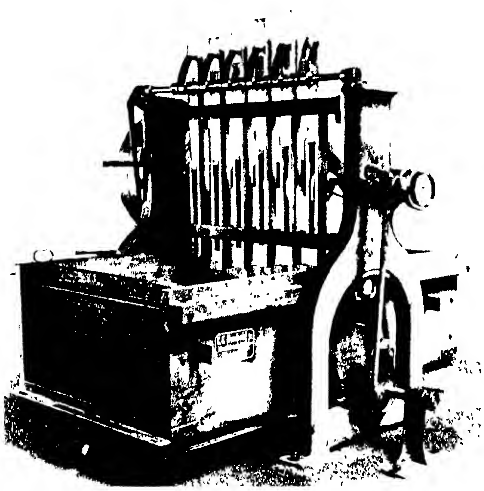


FIG. 241.—Stamping Machine for Bleaching and Washing Hosiery.

solution, is folded down in boxes or bins, and left undisturbed for from 2 to 3 hours, during which time the chemic solution acts on the cloth. Heavy goods naturally require a longer treatment than light-weight material. When the cloth has whitened up sufficiently it is next run through a washing machine, entering one end of the washer and being carried up and down over rollers in a spiral manner until it comes off at the other end of the machine. A good flow of fresh water must be continually running through the washer in order to remove as thoroughly as possible the excess of chemic, as well as the soluble products of the bleaching.

6. Souring and Washing in Bleaching Knit-goods.

After coming from the washer, the cloth is next led through a souring bath for the purpose of decomposing the chlorine compounds still left in the fiber. The souring bath may consist of either a dilute solution of sulfuric acid (vitriol) of about 1° to 2° Tw. strength, or of a solution of sodium bisulfite (antichlor). Usually 3 to 5 percent on the weight of the cloth will be required of antichlor. The antichlor is considered better than sulfuric acid, as it neutralizes more quickly and

completely the chlorine compounds in the fiber, and there is also less danger of injuring the goods; and, furthermore, the cloth is apt to be softer to the feel. After the souring operation has been completed it is necessary to give the cloth a very thorough washing with fresh water in order to remove completely all trace of acid or antichlor, for if any acid were to be left in the goods, it would cause a weakening of the fiber on drying.

After washing out all trace of acid it is generally the custom to soften the cloth by passing through a bath containing a mixture of soap and oil, or some specially prepared softener. In this treatment there is also introduced a small amount of blueing for the purpose of tinting the color of the bleach and throwing it off the yellow cast to a bluish tone. The cloth then passes through squeeze rolls, and without further washing is hydro-extracted and dried. The continuous process of bleaching is open to several serious objections. In the first place the chemic and sour baths have to be used rather strong, and fresh quantities of the strong chemicals have to be added from time to time as the cloth passes through the baths, in order to keep them up to a uniform strength. This is very liable to cause spots and streaks on the cloth by reason of its coming in contact with the strong chemic or acid. This is a very common defect to be found in this method of bleaching. Again, by its very nature, the process is uneven in its action, for the first end of the cloth coming from the chemic bath into the bin is the last end out into the washer, and consequently one end of the cloth gets a much longer treatment with the chemic than does the other end.

7. The Discontinuous Method of Bleaching Knit-goods.

In the second process of bleaching knit-goods in the roll, the chemic treatment is given by a different method. Instead of the goods being padded with the solution and then allowed to remain still for some time for the bleaching to take place, the cloth is run continuously in the liquor, and the goods are practically not exposed to the action of the air at all. This process is coming more and more into use on account of its superior features. In the first place, the sequence of operations is not interrupted; when the goods are first placed in the bleaching machine they are run through the different operations of bleaching, washing, scouring, and softening without interruption; that is to say, the goods do not have to be removed from the machine for any one of these operations. The following is the general method of procedure: After coming from the boiling-out kier, the goods are run over a reel in a so-called string-tub machine. This machine consists essentially of a wooden or cement tub provided with a large reel at the back and a pair of squeeze rolls at the front. The rolls of knit goods are made up into separate chains, usually about three rolls of from 40 to 50 yds. each to each chain, and machines varying in size from 8 to 20 chains are employed. The separate strings of cloth are run over the reel, down into the tub, and up to the squeeze rolls. Below the squeeze rolls are placed a series of finger bars or partitions for the purpose of keeping the strings separate and to prevent them from falling over

one another. The back of the tub must be so curved that as the cloth falls from the reel it will pile up evenly, and gradually fall downwards through the liquor in the tub. The front part of the tub is straight. The squeeze rolls and the reels should be so geared together that the reel runs slightly faster, so as to take up any slack in the cloth. The sequence of operations in bleaching in this form of apparatus is as follows:

(1) A good washing is given the goods in the kier, and also afterwards when they are placed in the machine and before the bleaching operation takes place.

The string of cloth is then run out from the kier over a reel and into trucks which are divided into several compartments, each com-

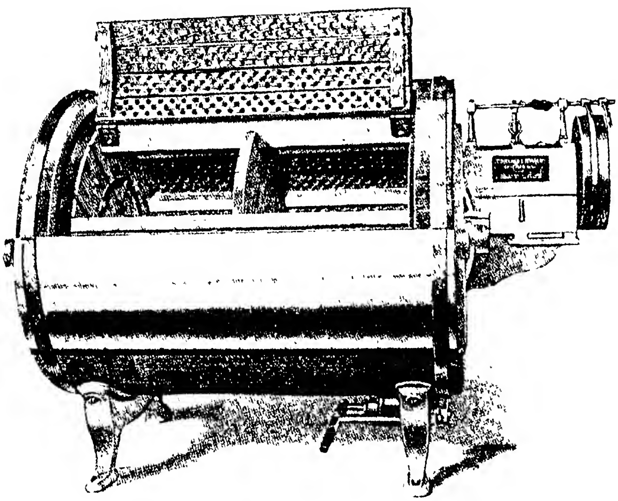


Fig. 242.—Cylinder for Washing Hosiery.

partment being of such capacity as to take care of one string for the bleaching machine. It is not well to allow the goods to lie too long in these trucks before they are run on to the bleaching machine and wet-out with water. Otherwise some parts of the goods are exposed to the air, and as there is more or less of the impurities still existing in the goods which have not yet been removed, there may be an oxidation by the air which will cause a certain kind of brown stain to form. If the goods are left too long, especially in the moist and warm condition, they will also be liable to the formation of mildew stains. As soon as the goods have been removed from the kier and placed in the truck the separate ends are run over the reel in the bleaching machine and the machine filled up. Sufficient water must be placed in the bleaching machine to ensure the proper running of the goods. This has to be guided by experience. Too much water will cause the cloth

to float on the surface and thus cause the strings to become tangled. Also, if too little water is present in the machine, the cloth as it falls down and folds over will pile up irregularly and the piles will fall over one on top of the other. This will also cause crossing of the strings and tangling. The proper amount of water will also depend on the weight of the goods, light-weight goods requiring a different volume of water from heavy-weight goods. This volume of water must in all cases be determined by actual experience in running the bleaching machine. It will be found to vary from a depth of 18 in. to 2½ ft., depending on the texture and weight of the cloth.

The goods now running in the machine are washed in lukewarm water for about 15 minutes before chemicking; and the cloth being in the open condition there is a better chance for the water to remove all the materials which have been decomposed in the kier. If there are any kier stains noticed it would be well to give the goods a preliminary souring; that is to say, the first wash-water should have a small amount of hydrochloric acid dissolved in it (1° Tw.), and be at a temperature of about 100° to 120° F. Kier stains in knit-goods may arise from a variety of causes. Usually they are due to impure water. If pure filtered water is employed there is usually no cause for kier stains unless colored cotton has been used in the make-up of the goods. Unfiltered water will nearly always give rise to trouble in the kier, either by reason of iron contained in the water which combines with the oil and alkalies to form a brown insoluble precipitate on the goods, or the stains may be caused simply by insoluble matter in the water, which is otherwise known as plain mud. It must be remembered that any kier is really a filter on a large scale, and the water which circulates through the kier is really filtered thereby, and any insoluble matter which may exist in the water will be caught up in the meshes of the goods. On this account all bleaching establishments should filter the water they use, for however pure the supply of water may be considered, there will always arise occasions when filtering is not only desirable but necessary.

For purposes of thorough washing in the string-tub machine, a water spray pipe should run across the entire machine just in front of the goods before they pass into the squeeze rolls. The water passing out through this spray under a heavy pressure will be forced thoroughly into the goods just as they pass into the squeeze rolls. During the washing, the drain valve should be allowed to be half-open, and fresh water should be continually admitted into the machine through the spray pipe while the dirty water is constantly running off.

(2) A treatment with chemic solution is given; this continues for about 40 minutes to one hour, and the strength of the bath varies from 1½° to 2½° Tw., depending on the weight and the character of the knit-goods. For heavy-weight goods containing yarns which are composed of rather low-grade cotton waste it will be necessary to use the stronger solution, for such cloth will be contaminated with a large number of motes or shives, or so-called "sticks," and these have to be removed by the action of the bleaching agent. For light-weight goods

composed of better yarns, it will only be necessary to run for a shorter time, and with a lower strength of the chemic bath. For heavy goods of low-grade waste yarn, the time of treatment should be for about 45 minutes cold, then the temperature of the chemic should be raised to about 110° F., and the goods run for about 15 minutes longer. This treatment with the hot chemic is necessary to decompose, bleach out, and destroy thoroughly the thicker motes in the yarn. For light-weight fabrics which are of a cleaner character, it would not be necessary to employ this hot chemic. Extreme care must be taken not to let the chemic solution go beyond 110° F., otherwise the oxidizing action of the chemic bath will be so great as to cause injury to the cotton fiber, and it will also make the goods harsh in feel as well as tender in strength. It will also be found that if the strength of the chemic is too great, or if the temperature at which it is employed is too high, instead of the goods becoming whiter in color they will acquire a yellowish cast.

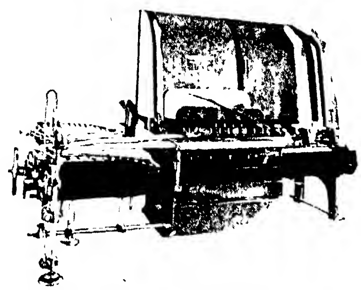


FIG. 243.—Drying Machine for Bleached Hosiery (Proctor & Schwartz).

(3) After the treatment with the chemic solution has been completed, a thorough washing must be given the knit-goods to remove all excess of the chemic and lime compounds. Fresh water is run through the machine continuously while washing by means of the spray pipes, the drain-valve being left partly open so that the wash-water may run off. This washing after chemicking must be very thorough, and be continued for at least 45 minutes or an hour. If insufficient water is employed, or if the washing is not continued for the necessary length of time, various faults in bleaching may easily arise; a great many defects in the bleaching of knit-goods may be traced to insufficient washing after the bleaching operation.

(4) After this thorough washing has been given, it will be necessary to give a treatment with "antichlor." This is nothing more than sodium bisulfite, which is used for the purpose of neutralizing the chlorine compounds. The amount of antichlor necessary to employ will vary from 3 to 5 percent on the weight of the goods, depending, of course, upon the quantity of chemic solution which has originally been used. The amount of antichlor, however, should be ample, and after the goods have been so treated they should not show the slightest test of any presence of chlorine. This test can easily be carried out by

pressing a piece of potassium iodide-and-starch paper on to the wet goods, or by moistening a portion of the goods with a solution of starch containing potassium iodide. The test paper of potassium iodide-and-starch is easily prepared by soaking strips of filter paper in a solution of starch containing some potassium iodide and allowing the paper to dry. This mixture of starch and potassium iodide is a characteristic test for the presence of even very minute quantities of chlorine. The slightest trace of chlorine when brought in contact with this reagent will develop a bluish to a black color, depending on the amount of chlorine present. The treatment with the antichlor solution is cold, and the time of running should be from 20 to 30 minutes. Sodium bisulfite is a very efficient antichlor by reason of the fact that the sulfurous acid it contains is readily oxidized to sulfuric acid, and since chlorine is a strong oxidizing agent, they mutually neutralize each other.

(5) A thorough washing is again given after the antichlor bath has been run off from the goods. It must be remembered that in this antichlor or sodium bisulfite there is considerable acid, and it is necessary to remove all such acid, otherwise various faults will arise. The washing after the treatment with antichlor, therefore, must be very thorough, and should be continued for about 45 minutes, employing a good flow of fresh water through the spray pipes and leaving the drain-valve from the machine partly open so that the cold water is continually running away.

So far as the bleaching operations proper are considered, this last souring or antichlor treatment completes the process. In many cases it will not be necessary to give any further treatment to the goods; but in some instances, especially where heavy and low-grade materials are used, it will be considered essential to soften the goods before they go to the cutting room. The softening is produced by running the goods in a bath containing soap, or a mixture of soap and soluble oil, or even a suitably prepared softener. If considered desirable, the cloth may also be blued or tinted in this final softening bath by the addition of the necessary amount of bleaching tint. This is for the purpose of changing the tone of the white, giving it a bluish cast, which by most persons is considered more pleasing to the eye. The use of tinting agents, however, is not to be recommended in general. They add very considerably to the bleaching difficulties of obtaining even and uniform goods. Furthermore, very frequently the tint which is employed is not especially fast, and after the goods have been stored for some time, they will lose this blue cast and return to their original color.

The advantage of this system of bleaching the cloth in string-tubs is that throughout the operation there is a uniformity of treatment through the whole length of the goods; and furthermore, the cloth is in the open and floats through the liquor, so that it receives a very thorough treatment. Consequently there is less danger of lack of uniformity of bleaching, and the color is more likely to be even throughout the entire fabric. There is also less danger of the various faults of

bleaching which we have considered in the other process. If properly conducted, and if the washings are very thorough, there should be absolutely no danger of the after-tendering of the goods, or of the development of a yellow color on storing.

8. **Bleaching of Cotton Hosiery.**

Hosiery is bleached in much the same manner as other forms of knit-goods, though special forms of machinery are required. The goods are usually made up into small bundles or placed in net bags and boiled-out in a kier. The washing and bleaching is usually conducted in a rotary drum machine. This consists of a tank containing the necessary liquor in which a perforated wooden or metal drum is rotated horizontally. The hosiery is placed in this drum and is thus carried through the liquor by its movement. The goods should be packed in the drum loosely enough to allow of the free penetration of the liquor. Usually rows of wooden pins are arranged in the drum so as to cause more or less movement of the goods within and keep the material in a well-distributed and open condition.

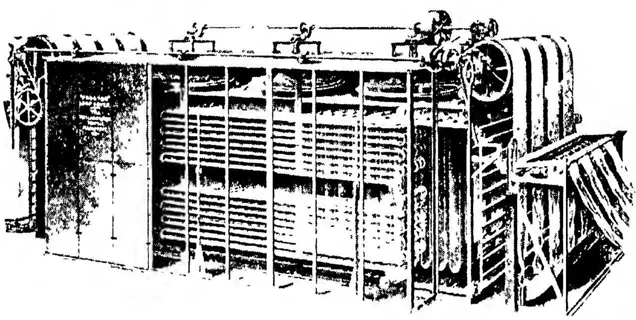


FIG. 244.- Loop Dryer for Knit-goods (Proctor & Schwartz).

A continuous washing and scouring machinery for hosiery is a recent English invention and operates on a different principle from the drum machine. Its general construction is shown in Figure 238. The scouring is performed in a long cast-iron tank, in which any suitable solution may be used, and of sufficient depth to cover the goods. The tank is about 25 ft. long and 4 ft. wide, and is provided with 22 fluted rollers, underneath which travels a galvanized brattice.

The goods are fed to this brattice over a feed table passing under a spray box, which well dampens the goods with a solution similar to that used in the tank. After being dampened, the goods are then taken forward by the traveling brattice and pass under the rollers. These latter are rotated by the passage of the goods, and, moreover, may be regulated as to their pressure by means of springs. Upon reaching the end of the tank the goods are delivered to another small traveling brattice which conveys them to a set of squeezing rollers. By

this means the bulk of the scouring liquid is removed and passed back into the tank. After passing through these rollers the goods are well sprayed with clear water, to wash out thoroughly any of the scouring liquid remaining, and passed between a second pair of squeezing rollers. This final squeezing removes most of the liquid from the goods and passes them in a damp condition to a small delivery brattice from which they are deposited into baskets or other suitable receptacles.[1]

One of the chief troubles to be experienced in the bleaching of hosiery is the occurrence of oil-stains. These stains are produced by the knitting machines, and especially in some forms of knitting where the thread is worked in oil, and this is particularly true of the reinforcement threads knitted into the heel and toe. In some mills, it is the custom to examine all hosiery before bleaching in order to sort out the oil-stained ones and these are dyed black. Instead of sorting out the stained hosiery, however, it is cheaper to process the goods previous to bleaching in such a manner that the oil-stains are removed. The following method is said to yield good results: For 100 lbs. of cotton hosiery, use 8 lbs. neatsfoot oil, 3 lbs. resin soap, and 6 lbs. soda ash boiled up in 35 gals. of water. The hosiery is put in a tom-tom machine and the solution is added with sufficient water to cover the goods. The machine is worked for 20 mins. and then the hosiery is taken out wet and thrown into the kier for boiling-out. This operation is conducted in the usual manner with either an open or a pressure kier. The chemicking or bleaching may be done in either a rotary or other machine as above mentioned, or it may be carried out in a bleaching cistern after the manner of what is known as the "still" bleach used

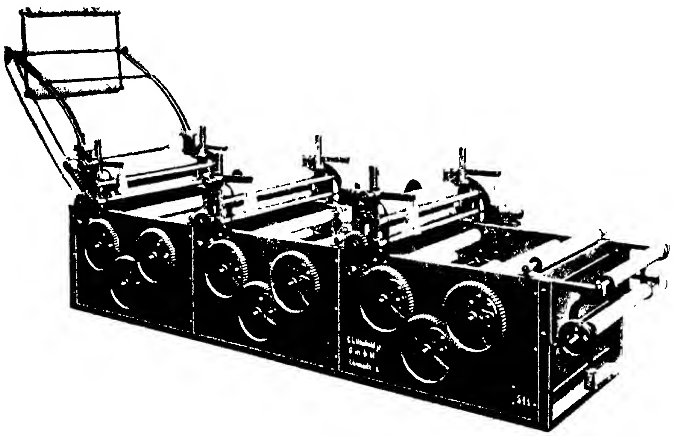


FIG. 245. Open Washing Machine for Knit-goods (German Type).

[1] This machine has a capacity of 45,000 lbs. of hosiery per week.

for yarns or warps. The cistern consists of a stone or wooden tank lined with cement and provided with a false bottom and a centrifugal pump for suitable circulation of the liquid from the bottom chamber of the cistern to the top. The hosiery must be carefully and evenly packed in the cistern in order to insure even circulation and to avoid channeling of the liquor. The chemic generally consists of a solution of bleaching powder or sodium hypochlorite of $1\frac{1}{2}°$ Tw. strength, and is contained in a cement tank below the bleaching cistern. By means of the centrifugal pump the liquor is raised from the lower well and is thrown over the top of the goods in the cistern by means of a perforated wooden tray. The bleaching liquor then percolates through the goods and runs down into the false bottom and thence into the well again. The bleaching solution is circulated through the goods in this manner for about two hours, then the circulation is stopped and the liquor is allowed to drain back into the well. The goods are then washed with water for half an hour, and next soured with sulfuric acid of $1°$ Tw. for another half an hour. The sulfuric acid liquor is contained in a second well similar to that for the chemic, and is circulated in the same manner by means of the pump. After souring the hosiery is allowed to drain for 20 minutes, then washed for half an hour. The goods are then taken out and put into a paddle tub where they are treated with a soap solution or suitable softener and blued. After this process the goods are hydro-extracted, stretched on forms, dried and finished. In certain cases of low grade yarns, it may be necessary to give two bleaching treatments with an intermediate boiling of the goods in a paddle tub with a weak solution of soda ash in order to obtain a satisfactory white color.

9. Bleaching of Colored Cotton Goods.

There is at present a wide range of cotton fabrics made with colored stripes or fancy patterns which are constructed by weaving in colored yarns together with unbleached white cotton yarns; and these goods are subsequently bleached in the piece for the purpose of clearing up the white part of the cloth. This character of fabric presents very special conditions with respect to bleaching, as it is necessary that the bleaching operations be so conducted as not to have the color destroyed or to have it run into the white.[9] There are only certain dyestuffs which will resist this bleaching effect, and these include such dyes as Turkey Red, Para Red (to a less degree), Indigo, Aniline Black, Cutch Brown and a number of the so-called vat dyes, such as the Hydron colors, Indanthrene, Ciba, Helindone, Algol colors, etc., as well as certain colors derived from Naphthol AS (the anilide of beta-oxynaphthoic acid).

The bleaching of colored cotton goods has of late years become a very important branch owing to the introduction and wide use of the fast vat dyes which are capable of giving colors that will resist the action of hypochlorite liquors. This field is also extended by the fact that modern laundry methods necessitate the use of hypochlorite liquors in the cleansing and whitening of cotton wash-fabrics. Fabrics

such as shirtings, ladies' blouse material, toweling, etc., are now largely woven with colored patterns, and these are bleached in the piece. Before bleaching colored goods, the bleacher should assure himself of the fastness of the colors used to the treatments he intends to employ, and this can be done by first running a small sample of the cloth through the various processes to be used as a preliminary test; it is not enough to rely solely on the resistance of the color to a test solution of hypochlorite.

The bleaching of dyed cotton goods is still a subject on which there is a large amount of information to be collected and properly correlated. The subject has not been studied in the full manner its importance demands. The manufacturer and dealer in dyestuffs has at best an imperfect knowledge of the conditions to which dyes are subjected in the processes of commercial bleaching; and, on the other hand, the dyer and bleacher are liable to act in rather a haphazard manner in carrying out the treatment of the goods, as they have very little accurate knowledge concerning the qualities of the dyestuffs available. The dyestuff maker usually considers that if a dye gives a color that will withstand fairly well the action of a weak solution of chloride of lime, it can be listed as fast to bleaching, whereas he may be entirely erroneous, as the color may bleed badly in the boiling-out process with alkali which is a part of the bleaching process. On the other hand, the bleacher is not enough given to devising suitable modifications of the bleaching process to meet the conditions due to the presence of colored yarn, while at the same time attaining the commercial result desired.

10. **Methods of Boiling-out Colored Goods.**

In the bleaching of colored cotton goods, it is necessary to avoid a strong boiling-out operation in the kier with caustic alkalies, as this, as a rule, has more effect on the colors even than the bleaching with a hypochlorite solution.

While in the market bleaching of white goods chief dependence is placed on a very thorough and severe boiling-out operation, it must be borne in mind always in the bleaching of colored goods that the boil-out process must be subdued to a minimum, and the chief reliance in the bleaching effect is placed in the chemicking or hypochlorite treatment. The vat dyes will only stand a moderate boil-out, though they may perfectly resist the bleaching action of hypochlorites. On this account the boil-out should not be conducted if possible under pressure, and strong caustic alkali solutions should be avoided.

It must be accepted as a preliminary condition that colored goods cannot be given as complete and severe a bleaching as plain white fabrics, as all of the operations have to be tempered to favor the preservation of the color. It is also unnecessary that the bleaching be as thorough as with white goods, because the presence of the color really calls for a different type of white than is the case with all white goods, and the effect is often much better if the bleach is not of too intense a white. Owing to the effect of color contrast, in many cases, even if a very high white were produced when viewed by itself, when seen in

juxtaposition with the color it appears tinted. The desire in bleaching colored cottons is chiefly to clean up the white parts of the fabric so as to remove dirt, motes, seed particles and the natural impurities of the raw fiber. If high-grade combed yarns are employed in the fabric it will not require very severe action to accomplish this cleansing, but if low-grade carded yarns contaminated with considerable motes, broken seed and leaf are used, it will generally require a more thorough processing to obtain a satisfactory result. In the older processes of bleaching where very prolonged kier-boiling was employed with milk of lime, caustic soda and resin soap, and also treatments with acid liquors, when it came to a question of bleaching cloth containing dyed yarns there was but slight sacrifice made in the methods of treatment, but various devices were used to avoid the severe action on the colored

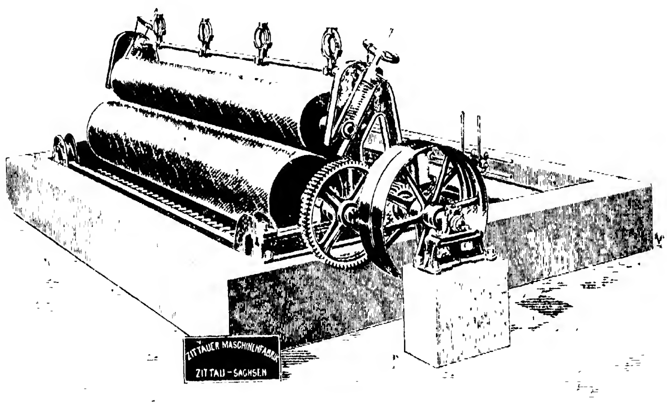


FIG. 246.—Slack Tension Washing Machine.

portions of the fabric. Frequently these colored parts were limited to headings which occurred at intervals through the length of the fabric, and it was the practice to "hang out," as it was called, these portions; that is to say, instead of running the colored part of the cloth into the kier a loop was made containing the heading and this was hung over the edge of the kier. This scheme, however, introduced various bad features, because in this manner some parts of the cloth received more treatment than others, and there was consequently an uneven bleach around the headings, and as the same system was practiced in the other processes of bleaching, such as the souring and hypochlorite treatments, it must have given a rather undesirable effect. And yet in the English system of bleaching this procedure seems to have long been the accepted one for this class of material. Such a method, of course, was not applicable to goods having continuous colored patterns all through the fabric, but only to such goods where the colored portions

came at intervals. The present methods of bleaching these goods have been considerably modified so that this character of bleaching has been widely extended now to include many cotton fabrics that formerly were not bleached in the piece, but had to be made from bleached and colored yarns.

11. Use of Malt Extracts and Diastase Enzymes.

A process which is largely employed at the present time is to remove as far as possible the starch and sizing materials on the cloth together with most of the pectin matters present in the raw cotton by a treatment with a suitable diastase product. This material contains an enzyme which has the property of quickly rendering soluble the starchy, gummy and pectin substances, and thus performs more or less the function of the caustic soda boil; and, at the same time, this enzyme action has little or no effect on the dyed colors in the cloth. The goods are first wetted-out by running through hot water or a dilute soap solution, or a soap solution containing also some soluble oil, such as Monopole or other suitable sulfonated oil. After this treatment they should be washed again in hot water to remove the excess of soap and oil, and then the cloth is impregnated with a solution of the enzyme preparation. This is usually done by running the goods through a box containing the solution with immersed squeeze rolls and then squeezing so as to leave about an equal weight of liquor as of cloth in the goods, and then folding the impregnated cloth down in bins and allowing to stand for eight hours, or conveniently overnight. Before the goods are run into the enzyme liquor care should be taken that they are free from alkali as the enzyme action is much reduced or altogether stopped by the presence of alkalies. If soda ash or any alkali has been used in the preliminary wetting-out, it is well to wash the goods subsequently in water containing a little acetic acid in order to assure complete neutralization.

There are several enzymes especially prepared for this process, such as Diastafor, Diax and Polyzime. The first two are prepared from malt, whereas the last one is made by the action of special fermenting organisms on bran. The enzyme solution should be used in a strength of about 1 to 2 percent, and in the case of Diastafor and Diax the liquor should be maintained at a temperature of from 120 to 150° F., whereas in the case of Polyzime the temperature of the enzyme bath should be held at about 110° F., as at higher temperatures the action of the enzyme is arrested. After the enzyme treatment the goods are washed thoroughly in hot water or in a hot dilute soap liquor to which some soda ash may be added according to its effect on the color.

12. Bleaching with Sodium Hypochlorite Solution.

The goods are then bleached by the use of a sodium hypochlorite solution which may be prepared either from the solution of liquid chlorine in caustic soda or by the electrolytic process, or by the interaction of a soda ash solution with one of chloride of lime. The bleaching liquor should be of a strength of about 1 to 1½° Tw. or have an

"active" chlorine content of 0.5 to 1 gram per liter. After bleaching the goods may be run through a bath containing a small quantity of acetic or formic acid and then thoroughly washed and finished.

13. Use of Special Kier Preparations.

There are some dyestuffs the colors of which will stand a fair degree of caustic soda boiling in a kier, although in such cases it is usual to add to the kier liquor a special preparation which will tend to prevent any action on the color, such as a preparation known as Ludigol. This product is the sodium salt of meta-nitrobenzene sulfonic acid. Anthraquinone sulfonate is also employed for the same purpose.[8] Inorganic oxidants are also used, such as sodium or potassium

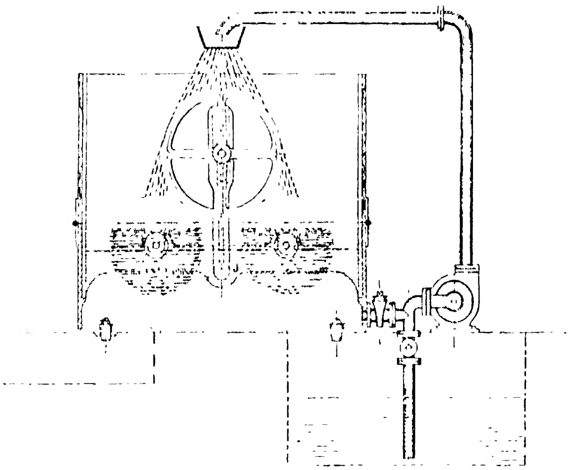


FIG. 247.—Chemicking and Souring Machine for Open Width Goods (Butterworth).

bromate,[9] salts of manganese, sodium bichromate, etc. The Farbwerke Höchst in a patent (1910) describe the use of manganese chloride. After being dyed with a vat color the goods are treated with a bath of manganese chloride of 7° Tw., squeezed and dried. H. Byk [10] suggests the use of sodium perborate for the bleaching of colored cottons, as in this case the sodium perborate may be used in connection with soap in a boiling bath. It is claimed that the effect on the colors in the kier-boil with the alkali is due to a reducing action brought about by certain products of decomposition through the action of the alkalies on the impurities and sizing materials in the cotton cloth, and this reducing action causes the vat dyes to be slightly dissolved from the fiber, and consequently has the effect of making the color bleed.

[8] *Ger. Pat.* 205,813.
[9] Hochst, *Ger. Pat.* 218,354.
[10] *Ger. Pat.* 250,397.

14. The Modification of Bleaching Methods for the Preservation of the Color.

In determining the bleaching fastness of dyestuffs, laboratory tests on the dyes are of very little value, as it is not possible to imitate satisfactorily in the laboratory the practical conditions of commercial bleaching. The only method of testing that is of value is to send a sample of the dyed color mixed with some white cloth through the regular bleaching processes as practised in the mill. There are only a very few colors that will completely withstand the usual treatment of bleaching; consequently it devolves on the bleacher to endeavor to modify his methods with a view of preserving the color, and at the same time producing a satisfactory bleach. It has been amply demonstrated as already mentioned, that the most severe action on the color is not in the bleach liquor itself, but in the alkali boil that is used to decompose the impurities in the raw cotton. Even the vat dyes will not satisfactorily withstand this treatment as ordinarily carried out in the processing of white goods.

15. Dyes Chiefly Used for Colors Fast to Bleaching.

Previous to the introduction of the vat dyes, there were a few special colors which were capable of withstanding the bleaching operations. The foremost of these probably was Turkey Red, but the manner in which the red was dyed had considerable to do with its quality of fastness for bleaching. The color obtained by the old Turkey Red process is faster to bleaching than that produced by the shorter and newer method, due probably to the better fixation of the oil. The character of the oil used in dyeing the Turkey Red also exerts considerable influence on the fastness of the color. That dyed with rancid olive oil is said to give a better result than the colors obtained by the use of ordinary Turkey-red oil. Also, if the dyed yarn is not thoroughly soaped after dyeing, it will show a tendency to bleed during the bleaching operations. Another color which was used was the blue obtained from Indigo. In light shades, however, Indigo is not at all fast to bleaching and at the present time there are vat dyes which are much faster in this respect than Indigo. Only the heavy shades of Indigo can be considered at all fast to bleaching, and even in this case the color shows a considerable loss. The manner of dyeing the Indigo on cotton also considerably influences its fastness to bleaching. If the shade is built up by a number of dips, a faster color will be obtained than with a few dips in a strong vat. Also in dyeing cotton with Indigo intended for bleaching, the yarn should first be boiled-out thoroughly in caustic soda in order to assist the penetration and absorption of the color, and before dyeing it is recommended to wet-out the yarn in a dilute bath of boiling sulfuric acid and then rinse thoroughly. If the Indigo in the vat is not properly reduced, if the vat is not clear working, if the color is not well penetrated but is only superficially deposited, if the color has been dyed too heavily in one dip and has not been properly built up gradually by a number of dips, if the washing and after treatment of the dyed yarn have not been thorough and

proper, any of these factors, as well as others, may vitally influence the bleaching fastness of the color.

Some dyers have the old fashioned opinion that the mineral pigment colors are faster to bleaching than the synthetic coal-tar dyes, but this is not necessarily the case, as some of the mineral colors are more or less stripped by hot alkalies, and others by acid liquors or hypochlorites. The chrome pigment colors, including yellow, orange and green, are not very suitable for bleaching fast colors, as many precautions have to be taken to prevent the color from stripping, and the white is seldom satisfactory. The chrome pigment colors can be well replaced by the corresponding alizarine and vat dyes. Greens and olives, in fact, can be best obtained by the use of Alizarine Yellow, Alizarine Blue and Alizarine Orange dyed on an oil-tannin-chrome mordant. The process is rather tedious but gives a more satisfactory color than a vat green, as the latter does not have any great fastness to bleaching. Bleaching fast green has also been dyed with Chrome Green topped with Indigo and shaded with Chrome Yellow; but the use of Chrome Green on cotton introduces many difficulties, and it is hard to produce satisfactory dyeings. Iron Buff is sometimes used for bleaching fast colors and gives good results if dyed by processes especially adapted to this purpose.

Aniline Black is another example of a color which may be dyed by numerous methods. The best method for bleaching fast color is a two-bath oxidation black, but even here considerable care and experience is necessary to produce a color which will stand up properly under bleaching, and the dyer can materially assist the bleacher if coordinated intelligence is applied to the problem. Many dyers tone Aniline Black with Logwood, Methyl Violet or other dyes, and of course in these circumstances such a color would be badly altered during bleaching.

There are some of the substantive cotton colors that have a moderate fastness to bleaching and are sometimes used for the manufacture of fast colored goods. Such dyes are Chloramine Orange, Chloramine Yellow, Chloramine Violet, Brilliant Geranine B and Primuline Yellow (which has been after treated with chloride of lime solution), and also the basic dye, Methylene Blue on a tannin-antimony mordant. Usually these dyes are employed in light shades, and in bleaching the white ground care must be taken not to use alkaline liquors, as this will cause the color to run. The chief difficulty of these substantive colors is the fact that they bleed out to some extent even in hot water, although they may be perfectly fast to the hypochlorite bleach liquor.

The following table exhibits a list of direct cotton dyes that may be considered as having good fastness to hypochlorite bleaching solutions, such as would be normally employed for the bleaching of colored cotton goods. There is also given the fastness of these colors to the action of a boiling solution of soda ash, the test being boiling for one-half hour in a solution containing 2 grams of soda ash per liter. A record is given of any change or alteration in the color as well as whether the color bleeds into the adjacent white cloth. It will be found that

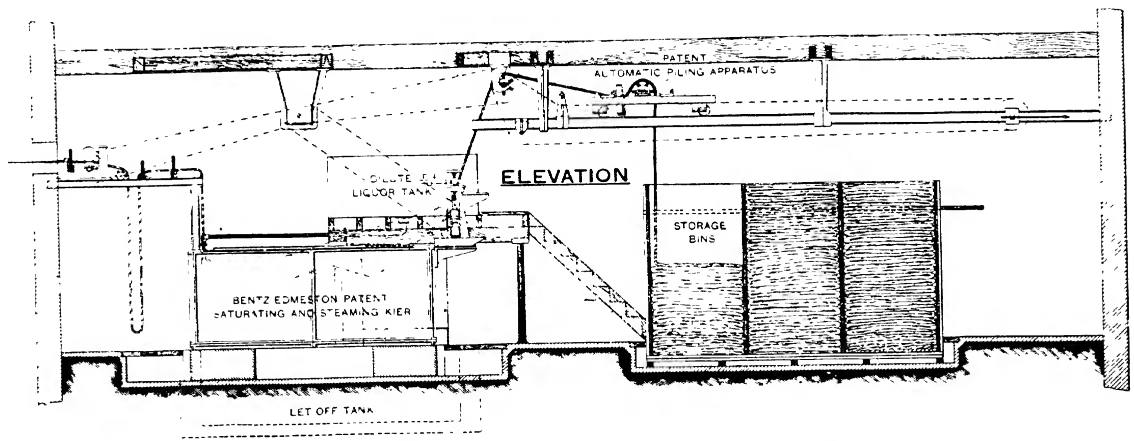


Fig. 248.—Diagram of Bentz-Edmeston System of Bleaching.

sometimes a dyestuff may be reasonably fast to the action of hypochlorite bleaching, and yet not be at all fast to alkali boiling, and therefore the bleaching of cloth containing such a dye must be adjusted to meet this condition. The fastness of Indigo is given for comparison.

Dyestuff	Fastness to Hypochlorite Bleaching	Fastness to Change in Color	Alkali Boil Bleeding to White
Primuline (after treated with chloride of lime)	excellent	no change	slight
Diamine Fast Yellow A	excellent	some loss	marked
Diamine Fast Yellow B	excellent	less loss	marked
Chrysophenine	excellent	much loss	very marked
Diamine Gold Yellow	excellent	much loss	marked
Diphenyl Citronine	excellent	much loss	marked
Diphenyl Fast Yellow	excellent	much loss	very marked
Polyphenyl Yellow 3B	excellent	some loss	marked
Aurophenine O	excellent	much loss	very marked
Oxydianil Yellow O	excellent	much loss	very marked
Chloramine Yellow	excellent	some loss	marked
Oxydiamine Yellow GG	turns brown	much loss	very marked
Mimosa	turns brown	some loss	marked
Hessian Yellow	good	much loss	very marked
Clayton Yellow	turns brown	some loss	very marked
Alkali Yellow R	turns brown	some loss	very marked
Mikado Yellow	excellent	much loss	very marked
Oxyphenine	excellent	slight change	marked
Curcumine S	excellent	some loss	marked
Chlorophenine Yellow	excellent	some loss	marked
Direct Yellow J	excellent	some loss	slight
Mikado Orange	excellent	much loss	very marked
Chicago Orange G	excellent	some loss	marked
Chicago Orange 3G	good	much loss	very marked
Chicago Orange R	good	much loss	marked
Chicago Orange 2R	good	much loss	very marked
Chloramine Orange G	excellent	some loss	very marked
Diamine Orange G	excellent	some loss	very marked
Brilliant Geranine 3B	good	great loss	very marked
Chlorantine Lilac B	good	great loss	very marked
Brilliant Rhoduline Red 3B	good	much loss	very marked
Direct Brown R	good	slight	marked
Direct Brown G	good	slight	slight
Mikado Brown B	good	much loss	marked
Mikado Brown G	good	some loss	marked
Mikado Brown M	good	some loss	marked
Heligoland Brown	good	much loss	very marked
Chicago Brown 2G	excellent	some loss	marked
Chicago Brown G	excellent	some loss	marked
Alizarine Red, old style	good	unchanged	none
Alizarine Red, new style	good	slight	slight
Azophor Orange	excellent	none	slight
Alpha-Naphthylamine Bordeaux	excellent	none	marked
Para Red	excellent	none	slight
Dianisidine Blue	good	slight	none
Azophor Black	good	slight	slight
Indigo (vat)	fair	some loss	none

16. Colors from Vat Dyes and Methods of Bleaching.

Besides the dyes given in this table there is, of course, the general class of vat dyes applied to cotton in a special form of hydrosulfite vat and these in general are fast to hypochlorite bleaching, and in many cases also of satisfactory fastness to the alkali boil. It must not be assumed, however, that all of the vat dyes are fast in these respects, or that all of them are possessed of an equal degree of fastness, for in some cases there is a great difference in the degrees of fastness. Any particular dyestuff should always be well tested by the dyer and bleacher before it is accepted for this purpose, as there is no general rule which may be laid down in respect to the qualities of fastness.

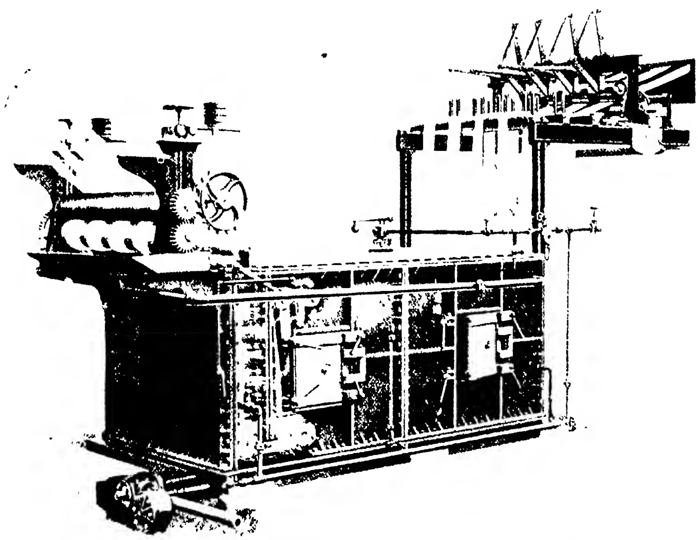


FIG. 249.—Special Kier, Bentz Process of Bleaching.

The Badische Company recommends the following method for the treatment of goods containing colors dyed with the Indanthrene series of vat dyes: When the cloth requires a boiling-out process under low pressure and the use of caustic soda lye, it is possible to prevent the ordinary bleeding of the colors by limiting the boil-out to a treatment on the jigger with a boiling solution of caustic soda to which is added 2 to 5 grams of Ludigol per liter of liquor. The Cassella Company, for the subsequent bleaching of cotton goods containing colors produced with Hydron Blue, recommends the following treatment: The cloth is boiled in the jigger with a solution containing 3 to 5 grams of Turkey-red oil per liter for 1 hour, then rinsed and treated for 1 to 2 hours in a solution of sodium hypochlorite at 1° Tw. in the usual manner, wash and sour for 20 minutes in hydrochloric acid

at 1° Tw. Finally run through a fresh bath containing a small amount of sodium bisulfite to act as an antichlor.

When an alkali kier boil is unavoidable, the Badische Company recommends the following method: For the boil-out liquor use 1000 parts of water, 16 parts of soda ash and 2 parts of Ludigol; or, where caustic soda is necessary, use the following: 1000 parts of water, 3¼ parts of caustic soda, 1¾ parts of soda ash and 4½ parts of Ludigol. The boiling is carried out for 3 to 5 hours in an open kier. The Farbwerke Höchst recommend the previous treatment of the material with a bath of dilute sulfuric acid, as follows: First impregnate with sulfuric acid solution of 1° Tw. and allow to lay for 12 hours, wash, boil-out in an open kier with 15 parts soda ash and 5 parts sodium bromate to 1000 parts water for 6 hours, wash, sour with sulfuric acid at 2° Tw., leaving in the acid bath for 3 hours, wash, boil-out

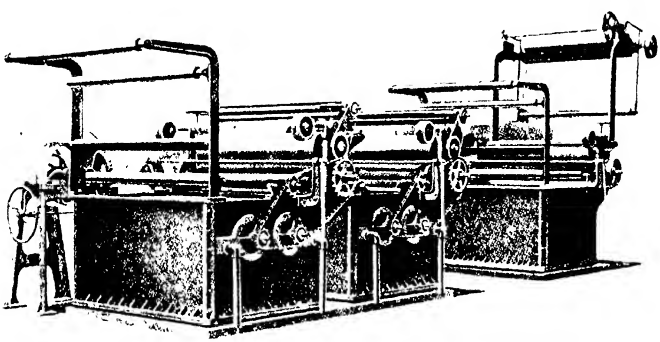


FIG. 250 —Washing, Chemicking, and Souring Range, Bentz Process of Bleaching.

a second time using 10 parts soda ash and 3 parts sodium bromate to 1000 parts water for 5 hours, wash, sour again with sulfuric acid for 3 hours at 1° Tw., wash, chemic in chloride of lime at 1° Tw. for 3 hours, wash, sour again in sulfuric acid for 3 hours at 1° Tw., finally wash thoroughly. In this process it would seem that the principal dependence is placed on the sulfuric acid treatments. Mohr [11] recommends the following process: After singeing, the goods are saturated with a solution of sulfuric acid at 1° Tw. and laid down in a bin for 12 hours, then wash and boil-out in a kier without pressure for 5 to 6 hours with a liquor containing about 7½ percent of soda ash and ½ percent of Ludigol or potassium bromate. The goods are then washed in a string tub washer and run into the chemic of chloride of lime or hypochlorite of soda, the strength of which must be adjusted in accordance with the conditions which may vary with the different kinds of fabrics and colors. After washing from the chemic solution and without souring, the goods are then run back into the kier and

[11] *Zeit. Farben-Ind.*, 1913, p. 40.

boiled again for 5 hours with a liquor containing 5 percent of soda ash and 1 percent of Ludigol or potassium bromate. A second chemic and washing is given and finally a sour in sulfuric acid of 1° Tw. By following out this general process with care it is said to be possible to use most of the vat dyes for the preparation of colored yarns in such fabrics.

For certain limited purposes where it is possible to avoid altogether a real boil-out operation and where a simple scouring in soap followed by a bleach with hypochlorite is sufficient, certain substantive dyes can be used, such as Brilliant Geranine, Chloramine Orange and Chloramine Violet, as well as Primuline diazotized and developed with chloride of lime, Dianisidine Blue and the basic Methylene Blue; with the intelligent use of this palette of colors a wide range of shades can be obtained.

17. **Bleaching Colored Goods with Peroxides.**

The use of peroxides for the bleaching of cotton goods containing dyed yarns is frequently practiced especially on high-grade fabrics and on fabrics containing wool or silk in admixture with the cotton. In fact, in the latter cases hypochlorites cannot be used, nor can alkaline boiling treatments be permitted as the wool and silk would be too much affected thereby. The bleach baths of either hydrogen peroxide or sodium peroxide are prepared in the usual manner as already fully described in preceding pages. Frequently the peroxide bath is also utilized for the boil-out process and the two operations are conducted as one. More commonly, however, the boil-out is dispensed with and a diastase treatment is given as already described, followed by washing and the peroxide bleach.

The use of peroxides in bleaching may have a different effect on the colors present than would be the case if hypochlorite bleach liquors were employed. It is, therefore, not well to assume that if a certain color shows proper fastness to hypochlorite bleaching it will necessarily have the same fastness towards a peroxide bleach. It is well for the bleacher himself to thoroughly test out a sample of the dyed color by subjecting it to the actual treatments he intends to employ. The vat colors, as a rule, will all be found of satisfactory fastness to proper peroxide bleaching. The alizarine dyes and many of the substantive dyes will also be found fast in this respect, although in the latter case bleeding may occur, not on account of the use of peroxide, but due to lack of fastness of the color to water. Most of the mineral pigment colors are also fast to peroxide bleaching.

18. **Bleaching of Printed Cotton Goods.**

This is a special phase of bleaching that really comes more under the subject of printing. When cotton goods are printed and then scoured in order to remove the thickener used in the printing paste, the color will frequently stain somewhat the white parts of the cloth. In order to "clear the whites" the goods are given a slight and rapid bleaching by running through a weak solution (¼° to ½° Tw.) of chlo-

ride of lime or a neutral solution of sodium hypochlorite. In the latter case the presence of free alkali should be avoided as otherwise alkali stains will be formed. After being slightly padded with the hypochlorite liquor the goods are usually run directly on to drying cans where the bleaching is completed and the chlorine compounds are used up and thus destroyed. In this method of bleaching it is necessary to be very careful to properly adjust the strength and amount of the hypochlorite liquor in the goods to avoid over-bleaching, the formation of tender spots and the destruction of the color on the printed parts of the goods.

In a patent of Kalle & Co.[12] there is described a method of bleaching cloth printed with vat or mordant dyes with the aid of an alkaline bleach liquor so as to brighten the white portion of the fabric without materially affecting the printed parts. The use of chloride of lime liquors alone for this purpose, it is claimed, bleaches out the color to too great an extent, but by addition of caustic soda to the chemic bath this bad effect is avoided in very large degree. The printed material is treated in a solution of bleaching powder or sodium hypochlorite of 1° Tw. containing 0.5 percent of caustic soda (40° Bé.). By the use of a solution of sodium hypochlorite alone even with an excess of soda ash present it is said the proper results are not obtained.

19. Bleaching of Lace Goods.

In the bleaching of lace goods the general scope of operation is practically the same as those for the usual form of cotton fabrics; on account of the make-up and delicacy of the fabric, however, it is not generally feasible to handle the goods in the rope form and they are usually folded up and made into loose bundles. Lace goods and nettings are frequently of a very dirty nature as they come to the bleachery owing to the graphite used in the lubrication of the machine bobbins during the manufacture of the fabric. As lace fabrics even in bundle form are of a light and spongy character they are easily penetrated in boiling-out and bleaching. A boil-out of 2 to 3 hours under moderate pressure is given with 2½ to 3 percent of caustic soda (on the weight of the goods). The kier should be brought to the boil quickly and in most cases be run for 3 hours, though in special cases a shorter boil may be advisable. In the treatment of lace goods it is customary to use smaller kiers than those usually employed in boiling of cotton cloth; also certain special forms of kiers may be used (such as the Mather-Platt or the Jackson) in which the lace bundles are placed in trucks and run into the kier and treated in that form, as this facilitates handling and preserves the goods from undue injury. As lace goods, as a rule, are made from hard twisted yarns, it is rather difficult to obtain good penetration if too large a lot is treated at any one time; this is true not only for boiling-out but also for the other processes of souring, chemicking, washing, etc. These processes are carried out in general in the same general manner as in the bleaching of other cotton goods, though it is sometimes necessary

[12] *Ger. Pat.* 233,211.

to employ a stronger chemic liquor or even to use it at a temperature of 90° F. to facilitate its action and penetration and to shorten the time so as to better preserve the fiber.

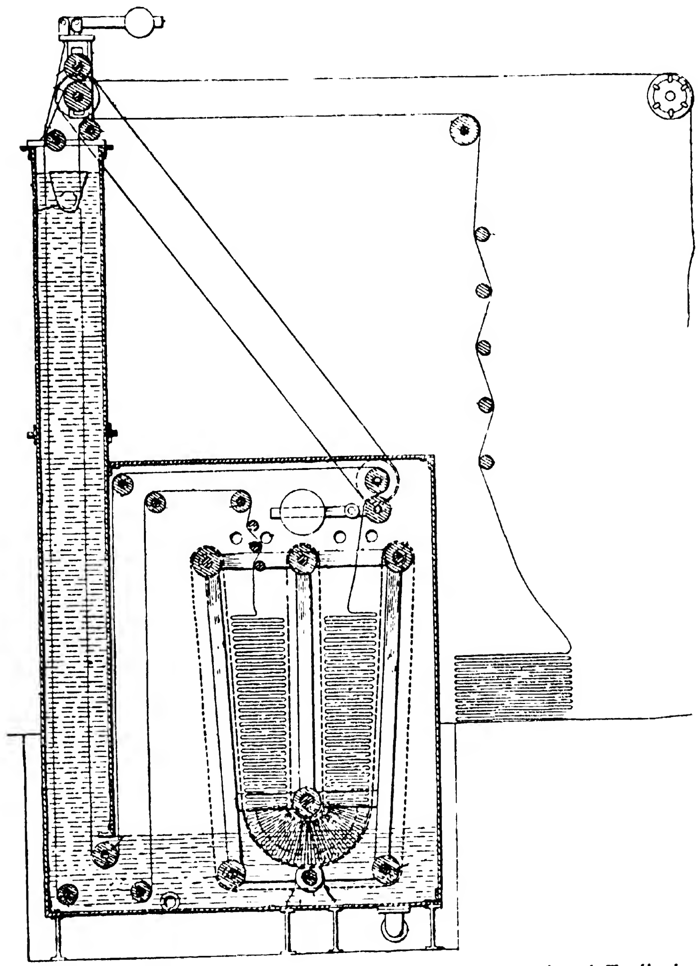


FIG. 251.—Continuous Bleaching System of Rigamonti and Tagliani.

20. Bleaching of Mercerized Cotton.

Since the introduction of the extensive use of mercerized cotton it has become a matter of considerable discussion as to just what are the best conditions for bleaching it. Mercerized cotton is prepared by treating cotton with strong solutions of caustic soda, the fiber being

maintained in a state of tension. As the treatment with caustic soda is really one of the operations in bleaching, it is claimed by some that it is cheaper and better to carry out the bleaching of the fiber with chloride of lime after the mercerizing. There are other authorities, however, who argue that the bleaching should be done previous to mercerization, in that the cotton is then in a clean and pure condition, and will readily absorb the caustic soda solution employed for mercerizing, and hence the latter operation is thoroughly and completely brought about. Another factor which is to be considered in favor of bleaching before mercerizing is that in so doing all the waxy and other natural impurities of the fiber are removed, as well as the dirt and grease which the yarn collects during the process of its manufacture. By a removal of these impurities, not only is the yarn better and more uniformly impregnated with the caustic soda solution, and a more uniform silky luster obtained, but also the caustic lyes do not become impure and weakened and may be used a greater number of times.

It has been advanced by some chemists that by the action of boiling caustic soda solutions and then treatment with bleaching powder, as is carried out in the bleaching of cotton, the fiber is rendered more or less unfit for mercerization by reason of the chemical action of the caustic soda and the chloride of lime on the cellulose of the cotton. If this were the case, good results would not be obtained by mercerizing bleached cotton, but, on the other hand, this does not appear to be so in actual practice, as it is claimed that even a higher luster is produced by mercerizing bleached cotton than by mercerizing unbleached yarn.

It is probably more customary, however, to bleach cotton after mercerization, both in the condition of yarn (either skein or warp) and piece goods. In the mercerizing of previously bleached cotton it is practically impossible to prevent discoloration of the material, consequently when bleaching is conducted subsequent to mercerization a better and cleaner bleach is obtained.

In the bleaching of mercerized material the bleaching operations may be conducted straight away after mercerizing without previously soaping or drying; the boiling-out operation may be dispensed with as the mercerizing process itself performs that function. The bleaching operations are carried out in the usual manner for skein, warp or cloth bleaching, the same series of processes and apparatus being used.

21. Bleaching of Union Goods.

In the bleaching of material containing a mixture of wool and cotton fibers serious difficulties are introduced owing to the radically different character of the two fibers, both with respect to the nature of the coloring matters present and the effect of the particular bleaching reagents employed individually for the separate fibers when treated alone. Sulfurous acid, for instance, which is an excellent bleaching agent for the coloring matter of wool, has little effect in bleaching the coloring matter of cotton; while solutions of hypochlorites which are universally employed for the bleaching of cotton, do not

have any bleaching effect on wool. It is necessary, therefore, to select as a bleaching agent for union goods one which will efficiently bleach both fibers simultaneously under the same conditions of treatment, and at the same time not materially affect the good qualities of either the wool or cotton. Of all the bleaching agents considered in this relation the peroxides (hydrogen peroxide or sodium peroxide) stand out as the pre-eminent choice.

Solutions of hydrogen peroxide bleach both cotton and wool quite effectively under practically the same conditions of treatment. Prac-

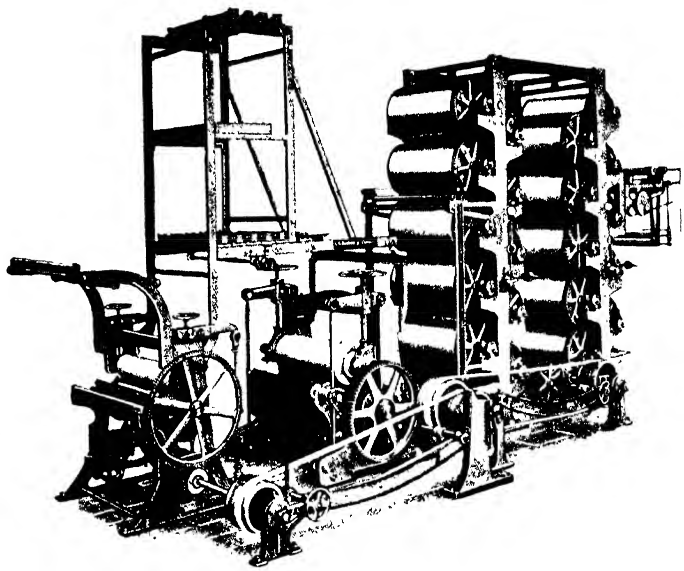


FIG. 252.—Chloring Machine, Water Mangle, Compensator and Dryer for Bleaching Printed Goods.

tically the same bath is used as that recommended for the bleaching of wool (see page 137). As a preliminary preparation for the bleaching it is necessary to thoroughly scour the material. It is not permissible in this case to boil-out the goods with alkalies as would be the case with all-cotton material, as under these conditions the wool portion would be seriously damaged. It is best to use a soap solution containing a small proportion of soda ash or ammonium carbonate. The goods are scoured in this bath at a temperature not exceeding 160° F. in order to avoid injury to the wool. As a rule, in the case of union fabrics it is not necessary to produce on the cotton as pure a white color as is desirable for an all-cotton fabric; for the wool at the best never bleaches to quite the same degree of white as the cotton, and

if the latter were bleached to a "high" white it would show up by contrast with the wool. This contrast of the two fibers is just the thing to be avoided in the case of nearly all union fabrics. Not requiring such a high degree of whiteness, therefore, it is not necessary to boil-out the cotton as thoroughly as would be the case where all-cotton goods are in question, and it will be found that the scouring treatment with soap and alkali will sufficiently remove the impurities from the cotton to permit of a satisfactory bleaching with the peroxide solution. In the bleach bath for union goods, of course, it is necessary to avoid the presence of caustic alkali the same as if wool alone were being treated on account of the sensitiveness of this fiber to the alkali. The peroxide bath, therefore, should be made alkaline in reaction by the addition of ammonia or of borax or perhaps of sodium silicate.

In the tinting of bleached union goods it is necessary to use precaution in the selection of a proper tinting dyestuff so that a uniform tone is obtained on both fibers, and in order to get this result it is necessary at times to skilfully manipulate the treatment with respect to temperature and character of the bath so that an even tone is obtained. Victoria Blue, Acid Violet, Methyl Violet, Soluble Prussian Blue are all used for this purpose, various mixtures being used to produce a desired tone of white.

In the bleaching of union goods where the warp is cotton and the wool is bleached with sulfurous acid by the stoving process, it sometimes happens that the cotton may be tendered. It is not the stoving itself that affects the cotton, but the cause of the tendering is often to be found in the residual soap that is left in the goods after scouring. Lloyd has shown, for example, that certain oils (the unsaturated or drying oils) absorb sulfurous acid, producing compounds which in time result in the formation of sulfuric acid. It thus happens that the sulfur dioxide used in the stoving may be converted into sulfuric acid by the fat of the residual soap in the fabric, and in this manner tendering of the cotton warp is brought about. It is clear that the inference from this is that the soap employed in scouring union goods previous to stoving should be made of oils of a non-drying character, and all traces of soap should be removed from the cloth by thorough washing before stoving.

Chapter XXIII.

Faults in Bleaching

1. Faults Arising in Bleaching.

The object in the bleaching of cotton cloth is to obtain a pure and uniform white color throughout the entire length of the goods, and furthermore this color should be permanent and not become yellowish on storing. There are, however, numerous faults which may arise in bleaching, the causes of which we will now discuss.

The bleacher has to reckon with many difficulties and defects, and very frequently the origin of faults is not to be sought in the bleaching itself, but in the weaving or elsewhere, as there are often defects in the raw cloth which only become apparent after the bleaching operations are finished. On the other hand there are also faults arising in bleaching which only show up in the goods after finishing or dyeing. It is too often the habit of the weaver to be careless in allowing the goods to become stained and spotted with the idea that these are easily removed by chemicking, and thus placing on the bleacher a needless burden. It is too frequently considered in the mill that "chemicking" will remove all kinds of defects and that the bleacher is the physician capable of administering a panacea for all ills which the goods may have acquired or have thrust upon them during the processes of manufacture. While it is often possible for the bleacher to remove or correct stains and spots, it also often happens that in doing so he is forced to employ chemicals or treatments which may in turn produce lack of uniformity or defects in finishing or dyeing.

A knowledge of the different kinds of stains, their origin, and the methods best adapted for their removal is very important in the education of the bleacher. Frequently the origin of defects is often a difficult thing to determine and requires some contact or experience with the previous life-history of the goods and a knowledge of the possibilities of faults introduced by the various manufacturing processes through which they have passed. From an economic point of view it is generally best to avoid the production of stains as far as possible rather than to rely upon the efficacy of bleaching to eliminate them. In most cases a chemical investigation, if carefully carried out by one experienced in the art, will explain the origin of the trouble; though frequently when applied to the finished goods without due reference to the condition and the method of processing the material in bleaching, such a chemical investigation may lead one far astray. It is seldom that the chemicals employed in bleaching are to be found present

in the finished cloth as they are (or should be) completely removed in the process. Nevertheless, certain faults may be due to the improper use of such chemicals, which fact, however, could not be ascertained with accuracy by a chemical examination of the finished goods, but would require an examination and checking-up of the bleaching process itself. Sometimes defects originate in purely mechanical causes, as

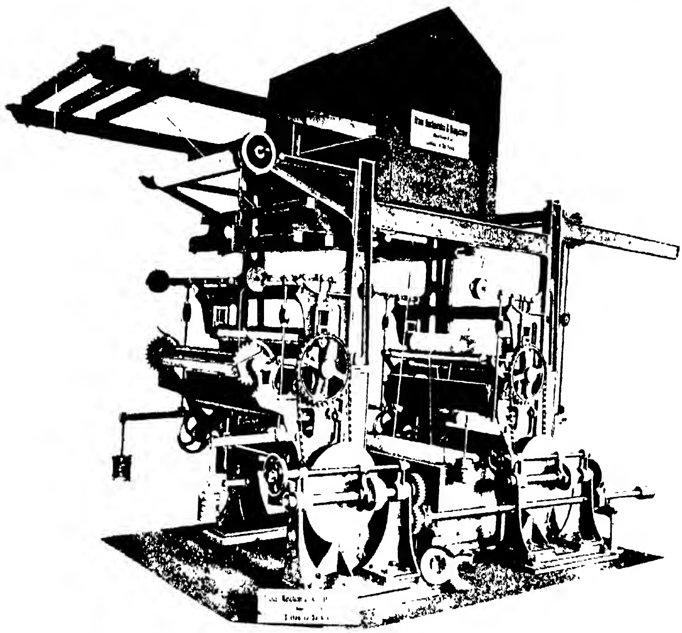


FIG. 253.—Apparatus for Chloring and Washing Union Goods to Clear White Cotton.

in inequalities of treatment resulting from defective machinery, such as worn and unsymmetrical rollers, faulty steam-pipes, defective calenders, leaky drying cans and numerous other possibilities.

In order to avoid subsequent trouble or blame, the bleacher should carefully examine the goods which he is called on to process in order to take notice of defects already present, such as dirty places and prominent oil stains, so that proper allowance may be made for their treatment.

2. **Faults Due to Uneven Weaving.**

Uneven results in bleaching may sometimes arise from the fact that different kinds or qualities of yarn are employed in the warp and filling; or different qualities of yarn may be found in the filling of

various pieces which will cause these pieces to assume a different tone of color on bleaching. Again, if fabrics are made from yarn which has already been bleached slightly, or "creamed," faults may also arise therefrom. Different qualities of cotton raw stock and improper blending may also be the cause of uneven colors. Such defects will usually show themselves in the form of straight streaks, bands, or lines running with the filling or the warp, as the case may be, exhibiting a slight difference in color or surface appearance, and becoming more apparent when the fabric is held toward the light. Slight differences in the count or twist of the yarn will also show up as similar defects in the bleached cloth. No precautions of the bleacher will obviate these defects inherent in the structure of the fabric, though finishing and sizing of the cloth will frequently cause them to become less apparent.

3. Stains Due to Tar and Asphaltum.

These are mostly present in the gray cloth and frequently arise from marks made on the ends of the pieces for purposes of identification and control. In some cases it is desirable to have these marks or numbers withstand the normal bleaching operations so as to carry throughout the identification of the pieces to the finished fabric. Under such circumstances the bleacher is not concerned with their removal though he should take the precaution to see that such marks do not bleed or smut off to other portions of the cloth. In cases where such marks are only desired to remain on the goods up to the bleaching operations, inks or crayons should be used which give marks capable of easy removal in the usual bleaching operations and without danger of smearing the rest of the cloth. In cases where the bleacher is required to remove stains of tar or asphaltum which have been inadvertently or improperly applied, it will be necessary to pick these out and give them a local treatment with turpentine oil, benzine, Tetrapol or other similar suitable solvent.

4. Mildew Stains.

In the air there are always present spores of micro-organisms that produce mildew when they become attached to a suitable culture medium, such as may be found in cotton cloth in a warm damp condition. The sizing present in the yarn furnishes a fertile ground for the growth of these fungus-like organisms; therefore it is not safe to leave the damp material exposed in a warm room for any length of time. Sized or even raw cotton cloth containing starch, gums or albuminous substances is especially liable to become stained with mould and mildew. Bleached cloth without finishing materials is not very subject to this defect, as the pure cotton itself does not afford a proper food for the development of the organisms. Mildew or mould may be caused by a variety of organisms and the stains resulting therefrom may be of different colors, such as yellow, red, green or black. The shapes of the stains may also be various, though these are mostly round. The formation of mildew in bleached and

sized cloth may readily be prevented by the addition of a small amount of a suitable antiseptic to the finishing materials. The chief antiseptics used are salicylic acid, zinc chloride, sodium bisulfite, boric acid and formaldehyde. Isolated mildew spots may be removed by scouring with a preparation such as Tetrapol and rinsing in warm water; also a treatment with citric acid is efficacious in many cases. Where the spots are strongly colored a treatment with perborate is recommended by Kind.

Mildew stains are easily recognized by their peculiar musty odor, and the vegetable growth may easily be observed under the microscope.

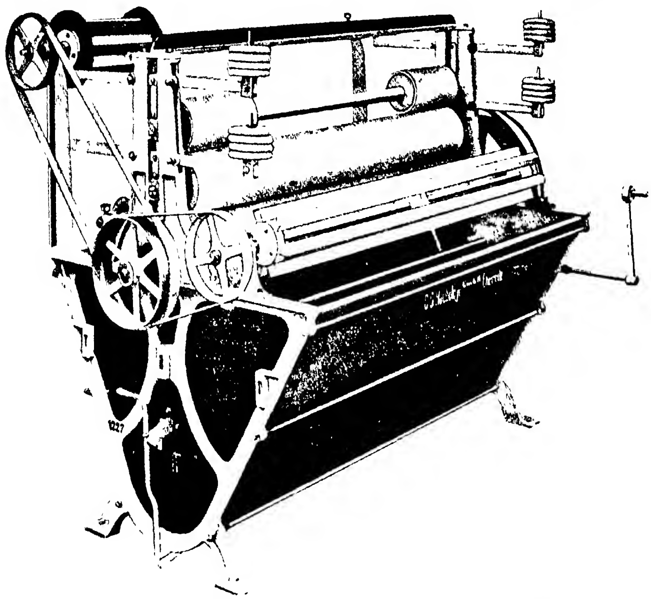


FIG. 254.—Soaking, Soaping and Washing Machine for Curtains, Embroideries, etc

Dry rooms and good ventilation are the best preventatives of mildew.

Mildew generally does not become apparent until the goods are nearly finished in bleaching. To get rid of mildew requires a good lye boiling and a strong chemic, with a thorough washing.

Fermentation will sometimes arise in fabrics due to the gum, grease, and resinous matters of the fibers dissolving in hot water in the steeping operations. These substances will rapidly engender fermentation, with the result that the goods will become tendered, and usually the damage will not show up until after the material has been bleached. Fermentation may be stopped by boiling, or better by treatment with a weak bleach liquor.

Wet wood is often covered with fungus similar to mildew which is readily transferred to the cloth. Spots caused by resinous matters from pine wood will disappear in the treatment with alkaline liquors.

5. Stains Due to Singeing and Heating.

These are usually yellowish brown stains caused by local overheating of the fabric during the process of singeing. These stains usually disappear in the bleaching. Sometimes smoky flames in the singeing machine will cause a streak of sooty discoloration.

Yellowish stains on hot calendered cotton goods are sometimes caused by faulty bleaching. These stains are of a brownish yellow

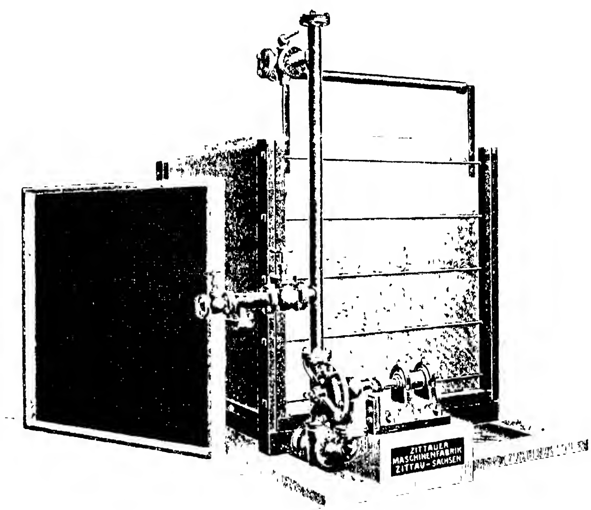


FIG. 255.—Chemicking and Souring Apparatus for Small Goods.

color and are distinctly noticeable when the goods come fresh from the calender, and they usually fade to a yellowish tinge after long standing in the air. Investigation in many cases has shown that cloth in which these stains are developed has been bleached in a chloride of lime liquor, and then folded down in piles exposed to the air. On standing in the air in contact with the chloride of lime solution, there is liability of having portions of the cloth become more or less dried by evaporation. Under such conditions the bleaching liquor in the cloth will become quite concentrated, and in consequence may act on the cellulose of the fiber, converting it into oxycellulose. On application of heat to these places the decomposition of the fiber is rapidly brought about, leading to the brownish discoloration as well as a weakening of the fiber.

That oxycellulose exists at these stains may be proved by testing the fabric with Fehling's solution.

6. Water Stains.

In order to have faultless bleaching the first essential is to have an adequate supply of good pure water. Dirty turbid water should never be used for bleaching as the impurities in the water will be taken up and absorbed by the cotton, giving rise to various sorts of yellowish

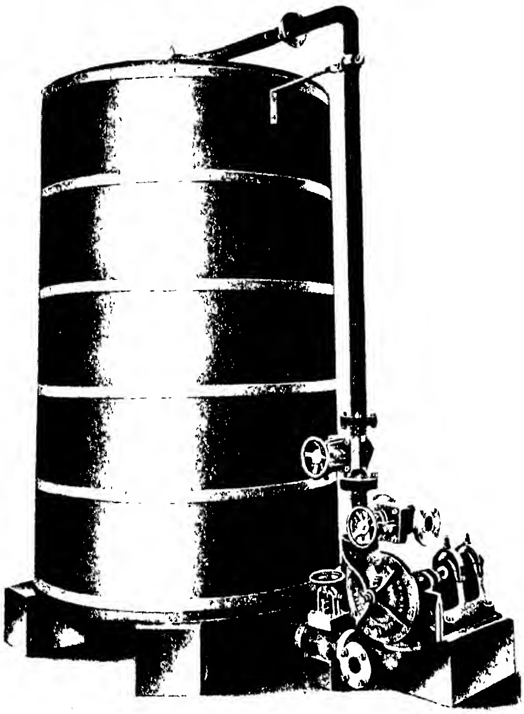


FIG. 256.—Bleaching Vat for Lace, etc.

and greenish stains. By proper filtration it is usually possible to obtain a clear pure water free from sedimentary impurities including both mineral and insoluble organic matter. Contamination with much organic matter, either insoluble or dissolved, usually causes yellowish stains on the goods. Hard water (although clear and colorless in appearance) may sometimes lead to water stains by reason of the calcium and magnesium salts forming greasy insoluble precipitates with soap solutions which may be used for softening the bleached cotton. These

insoluble metallic soaps on being heated (in contact with drying cans or calenders) may turn a yellowish or brownish color. The difficulty with this character of stain is that it does not appear until the goods are finished. Water containing dissolved iron salts (which are very likely to occur in water containing much soluble organic matter) is also liable to cause stains. Stains of this nature usually require a treatment with a dilute solution of hydrochloric or oxalic acid for their removal.

The use of hard water in connection with soap solutions in the washing or scouring of cotton goods is sometimes a cause of subsequent yellowing of the bleached material. The general properties of hard water and the effect of the calcium and magnesium salts producing the hardness on soap solutions have already been discussed in a previous chapter (see page 47). In the bleaching of cotton fabrics the use of hard water is perhaps not quite so objectionable as in the scouring of wool and silk; nevertheless there are certain features in this connection which it is well to bear in mind. It is said that the nitrogenous or protoplasmic constituents of cotton are changed by boiling with hard water into less soluble compounds,[1] which consequently become more difficult to remove by the soda boil, and which, if left, afterwards absorb chlorine in the bleach and thus may cause subsequent trouble.[2] In cases where soap solutions are employed in connection with cotton bleaching it is well to remember that though calcium and magnesium soaps are nearly all white when freshly prepared by precipitation, when they are dried and aged they often develop a yellowish or brownish color, the depth of such color depending considerably on the oil from which the soap has been made. The magnesium soaps are often more colored than those of calcium. If these soaps become fixed in the cotton fibers, the goods may appear all right when nearly finished, but may develop a color on keeping. This fault is the more likely to occur when the hardness of the water is due to magnesium,[3] both on account of the more marked color of the magnesium soaps and also to the comparative slowness with which the magnesium hardness is decomposed by soaps.[4] The gradual decomposition of the lime and magnesium soaps of oils whose fatty acids have a distinctive odor, such as cotton-seed or soya oil, is often accompanied by the odor of the oil. Resin soaps also tend to develop color, consequently soaps containing rosin are particularly unsuited for use with hard water. When it is necessary to employ a hard water only soaps whose fatty acids are of a light color should be used, while with soft water many cheaper colored soaps are comparatively safe.[5]

[1] The effect of hard water in the soda boil is shown by the following tests: Equal weights of cotton were boiled with soda solution made with distilled water and with water containing 40 parts of permanent hardness per 100,000. The soaps and nitrogenous matter present in the extract were then determined, in each case it was found that the use of hard water caused less oil and nitrogenous substances to be extracted from the fiber

[2] Trotman and Thorp, *Principles of Bleaching and Finishing Cotton Goods*, page 52

[3] Magnesium hardness differs somewhat from that due to calcium in that it is rather slowly decomposed by soap, and hence is more dangerous (Trotman and Thorp, *ibid.*, p. 52).

[4] Trotman, *Jour. Soc. Chem. Ind*, 1905. p. 267.

[5] It may readily be seen that when washing with hard water is carried out after treatment with soap, the soap residues, instead of dissolving and being removed by the water, are decomposed and deposited as lime and magnesium soaps in the fabric. The difference between

Sometimes the waters used in connection with bleached cotton may contain sodium chloride or sodium sulfate, and if these substances are left in the fiber to any material extent the finished fabric will feel damp. This is due to the fact that these salts are hygroscopic[6] It is frequently stated that the presence of sodium sulfate or chloride in water reduces the lathering power of soaps, but experiments made by Trotman do not confirm this view; on the other hand, however, they do actively hinder pedesis. They also inhibit to a marked degree the hydrolysis and removal of the impurities of cotton by the caustic soda boil.

7. Oil and Grease Stains.

These usually occur as contaminations on the raw cotton cloth, having been picked up in the weaving or other mechanical processes. Oily yarn stains are also often to be noticed appearing as short thin straight dark lines following the thread. These stains are usually due to mineral oil used in machinery lubrication. Fresh oil stains are not so difficult to remove, but when once dried into the fiber the difficulty of cleaning is much increased.[7] The oil as it gets on the yarn or cloth is usually mixed with fine particles of iron and carbon which leave a dark stain on the material even if the oil itself is removed (as by a solvent). If the cloth has been singed the oil spots will be more or less decomposed into tarry matter and carbon. Oil spots are usually removed in the kier boil, but if of such a character as to resist the alkali treatment special preparations must be used, either as additions to the kier or by subsequent treatment. Thies suggests the use of a mixture of 3 parts of mineral oil and 10 parts of vegetable oil as a lubricating mixture in order to prevent the formation of difficultly removable stains. Scheurer recommends the use of olive oil and paraffin oil as an addition to the kier for the purpose of removing oil stains.

goods scoured with hard and soft water can always be detected by analysis, for the former will contain from 0 3 to 0 5 percent of fixed fats, whereas the latter will only contain a trace of such compounds (see Trotman and Thorp, *Bleaching and Finishing of Cotton Goods*, p 53).

[6] Experiments were made by Trotman on finishing three pieces of the same fabric with distilled water and with water containing 17 grains per gallon of sodium sulfate and chloride respectively. After drying and exposing to the air for several days the moisture content was then determined to be as follows: (1) 3 85, (2) 7.50, (3) 7 00 percent respectively

[7] For the removal of mineral oil stains from calico in bleaching, Schweitzer recommends the addition of aniline or phenol to the soda lye According to this process the best results are obtained by using small quantities of aniline oil or phenol which may be dissolved readily in a soap solution The cloth is steeped in a solution containing 6 quarts of aniline oil, 25 gallons of water and 10 pounds of soap before being run into the kier It is said that 3 gallons of aniline oil will be sufficient to treat 4000 pounds of cloth. According to Saget (*Rev. Gen Mat. Color.*, Feb, 1901) the same result may be attained by the use of Turkey-red oil and then steamed without pressure The Turkey-red oil may also be added to the contents of the kier, whether this consists of lime, soda ash or caustic soda One gallon of the oil per 500 gallons of caustic soda solution of 2° Tw. are said to be sufficient Where soda ash is used the oil is added like resin soap, and when lime is employed, the oil is added to the lime after slaking, and the use of the oil with the lime boil is said to give better results than with caustic soda. For the preparation of such a liquor, slaked lime is mixed with its own weight of the oil, and then diluted with water; a milky liquid is thus obtained which settles very slowly, and if the solution is warm it will penetrate the cloth in a very perfect manner. In addition to the removal of mineral oil stains, cotton bleached with the aid of Turkey-red oil is much softer in feel, and it is claimed that the chemicking is rendered easier and more rapid. An addition of sodium bisulfite may also be made in conjunction with the above process In this case an amount of sodium bisulfite (30° Bé.), equal in weight to the Turkey-red oil employed, is added to the oil and lime mixture prepared in the manner above described. The cloth is passed through this liquor at 130° F. and then run into the kier and steamed under pressure. In this connection care must be taken to have all air expelled from the kier by steam, otherwise there will be danger of tendering the fiber.

A mixture of equal parts of shale oil and olive oil (or rape seed oil) is said to give good results with either the lime or caustic soda boil. The addition of a small amount of soap to the kier is also to be recommended as being quite efficient. Oil stains have always been the *bête noir* of the bleacher, and many suggestions have been made as to methods for their prevention and removal. It is now becoming more and more the custom of mills engaged in the spinning and weaving of cotton yarn and cloth for white goods to make a careful study and selection of the lubricating oils that are used on the bearings of the different machines. In cases where it is well-nigh impossible to so arrange matters to totally prevent accidental and occasional contact of the material with oil, it is recognized as a necessity to select a lubricating oil that is a suitable mixture of vegetable and mineral oils, so that the resulting stains are easily and completely removed in the kier boil.

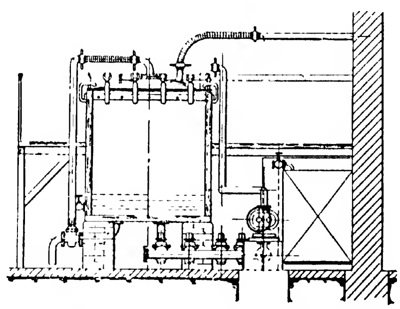


FIG. 257.—Bleach Vat for Small Wares.

Such oils should always be used in spinning and weaving machinery. Greater care is now also exercised in the prevention of oil drippings from overhead shaft bearings by the use either of suitable drip pans or of special forms of bearings and oil cups which are so designed as to eliminate all possibility of dripping. Since the proper recognition of the great saving effected in the elimination of oil stains, this disagreeable feature has been largely done away with at the present time. For the removal of very persistent oil stains it has been recommended to use small quantities of aniline oil or phenol (carbolic acid) as additions to the kier liquor,[8] but though experiments have indicated that such a treatment is very successful it does not seem to adapt itself to practical use. Saget recommends the impregnation of the cloth with Turkey-red oil, steaming, and then boiling in the kier. Also effective results may be obtained by the addition of the Turkey-red oil directly to the kier liquor. Grandmougin suggests the use of a mixture of Turkey-red oil and resin soap as an addition to the alkali boil in the kier. Other preparations recommended for the same purpose are Monopol Soap, Iso Soap, Turkone Oil and Tetrapol (a combination of soap and carbon tetrachloride).

[8] *Ger. Pat.* 88,432.

8. Kier Stains.

By far the most common stains occurring in bleaching are those produced in the kier. These are usually yellowish or browish stains and are due to the local accumulation of the precipitated pectin matters from the spent kier liquor. They are frequently due to uneven packing or the sudden chilling of the liquor by coming in contact with cold water. Such stains are more liable to occur at the top of the kier by the filtering out of the impurities in the kier liquor as it is circulated through the goods. These stains are usually easily removed in

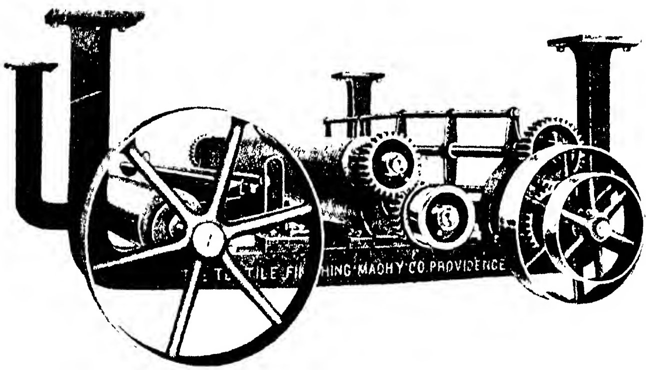


FIG. 258.—Scutcher for Opening Goods in Rope Form (Text. Fin. Mchy. Co.).

the subsequent processes of chemicking and souring and unless present in great amount and intensity are liable to cause but little trouble. If, however, these precipitated pectin matters become overheated or dried they then become quite firmly fixed in the goods and are rather difficult to completely remove. Other kier stains may be caused by rust on the sides or bottom of the kier; these are usually of a reddish brown color and show the presence of considerable iron. Treatment with dilute hydrochloric or oxalic acid will usually remove stains of this character; though if the stain has become dried into the fabric it may then offer considerable resistance to removal. Another form of kier stain may arise in the lime boil where milk of lime is used and undissolved particles of lime may become enmeshed in the goods. These may cause so-called "burnt" spots which are brown in color and show a weakness in the fiber; also such stains are limited to small spots. A further variety of kier stain may arise from the formation of oxycellulose in the kier boiling due to the presence of air in the kier. The oxidation of the fiber causes a gradual break-down in its structure leading to weakness and the formation of light yellowish or brownish stains which generally do not develop until the goods have been stored for some time (often several months). It is frequently

very difficult to determine just the exact cause of this kind of stain or discoloration. It is easy to determine the presence of lime (by an ash test), but it is not always possible to determine if the oxycellulose was formed in the kier treatment or in some of the subsequent processes of bleaching. Treatment with a boiling dilute solution of caustic soda or soda ash will usually remove the greater part of these stains, and also (strange to say) considerably strengthen the tender places in the injured fiber.

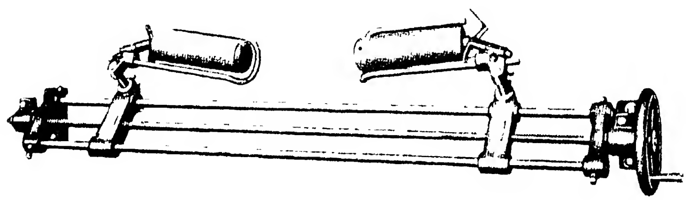


Fig. 259—Bolt-on-Guider for Goods in Bleaching (Text. Fin. Mchy. Co.).

9. Resin and Alkali Stains.

Occasionally yellowish stains are to be found on goods where resin soap has been used in boiling. These are caused by metallic salts in hard water precipitating resin soaps. Hardness due to magnesium salts will give darker resin stains than that due to calcium salts. Impurities in caustic soda or soda ash used in the kier may also cause stains. Lauber gives an example of reddish stains on boiled-out goods caused by manganese compounds in the caustic soda used. Uneven streaks or stains on bleached goods that are subsequently dyed may occasionally be due to highly concentrated caustic soda liquors coming in contact with the goods in the kier and producing irregular and partial mercerization. As the mercerized fiber dyes up a darker color streaks will result where mercerization has taken place.

10. Rust and Iron Stains.

These have a characteristic reddish or brownish color and may be identified by the ferrocyanide test (moistening with a drop of pure hydrochloric acid followed by a drop of potassium ferrocyanide solution, when a blue color will result in the presence of iron). These stains are often produced by allowing the moist goods to lie in contact with iron surfaces such as steam or water pipes, iron kier gratings, iron bolts, etc. To prevent iron stains from the kier, all the iron surfaces in the latter which come in contact with the goods should be given a coat of whitewash from time to time, or the kier may be lined with coarse cloth. Care should be taken, however, never to allow the boiled-out goods to remain unnecessarily long in the kier. Rust stains may also get on the goods from water which has lain a long time in the pipes. When starting operations at the beginning of the week, for example, the water first drawn may often be contaminated with sludge of iron rust, and care should be taken not to allow this to

be brought in contact with the goods. Also condensed water (which is practically distilled water), or even very soft water if stored in iron tanks or pipes, will rapidly dissolve a relatively large proportion of iron, which will subsequently separate out as a sludge of iron rust and if proper care is not observed bad stains are liable to arise. Iron stains which have been freshly made will usually disappear in the bleaching and cause but little trouble. Old iron stains, however, which have dried into the fiber offer considerable resistance to removal. The difficulty of getting rid of iron stains is also complicated if accompanied by oil and grease, as is often the case. The best treatment to adopt is to use a bath of warm dilute oxalic acid or a dilute bath of sodium bisulfite. Dilute hydrochloric acid (1° Tw.) may also be employed with good results in many cases. It is also stated that treating the stains with a rather concentrated solution of sodium bifluoride will remove even the most resistant rust without injury to the fiber. When the rust stain is combined with oil it is recommended to treat with a hot solution of 1 part of neutral soap, 1 part of glycerin and 3 parts of water.[9] Another process recommended for the removal of old iron stains is to first treat with an acid solution of potassium ferrocyanide which will cause the formation of Prussian Blue; a treatment with caustic soda solution is next given which will convert the blue into freshly formed iron hydrate, and the latter is then easily removed by dissolving in dilute hydrochloric acid. Burmol (a hydrosulfite preparation) is also recommended for the removal of rust stains; it is used in a lukewarm solution and is usually applied locally.

11. Lead Stains.

These may arise at times in the case of goods bleached with hypochlorite liquors in contact with lead surfaces, such as pipes or lead lined apparatus. Hypochlorite liquors, especially in the presence of air in contact with lead, produce a dark brown lead peroxide which is readily absorbed by the cotton. Kiers or kettles used for high pressure boiling with caustic soda should not be lined with lead. Lead stains should be treated with hydrochloric acid and well washed.

12. Stains Due to Oxycellulose.

Probably the chief defect to be met with in bleached goods is that due to the formation and presence of oxycellulose. As already described in previous pages this can arise by oxidation of the cotton cellulose both in the alkali or lime boil in the kier and in the bleaching processes with hypochlorite and acids. The formation of oxycellulose not only leads to a tendering of the fiber, but also causes yellowish or brownish stains to develop on storing. The prevention of such stains necessitates a very careful attention to the details of both boiling-out and bleaching, and very frequently it is a matter of extreme difficulty to locate the exact cause of the trouble. The brown color due to oxycellulose may generally be either completely or very materially removed by treating with a hot dilute solution of caustic soda. The lack of

[9] Weber, *Jour. Soc. Chem. Ind.*, 1892.

proper removal of all traces of hypochlorite or free chlorine or acid liquors from the cotton is a frequent cause of the formation of oxycellulose (or hydrocellulose) and the production of subsequent stains. All bleached goods should be carefully tested to ascertain if such chemical residues are present. Traces of acid may be tested for with Congo Red (either the test paper or the solution), which turns blue or black in the presence of mineral acids. Free chlorine may be detected by

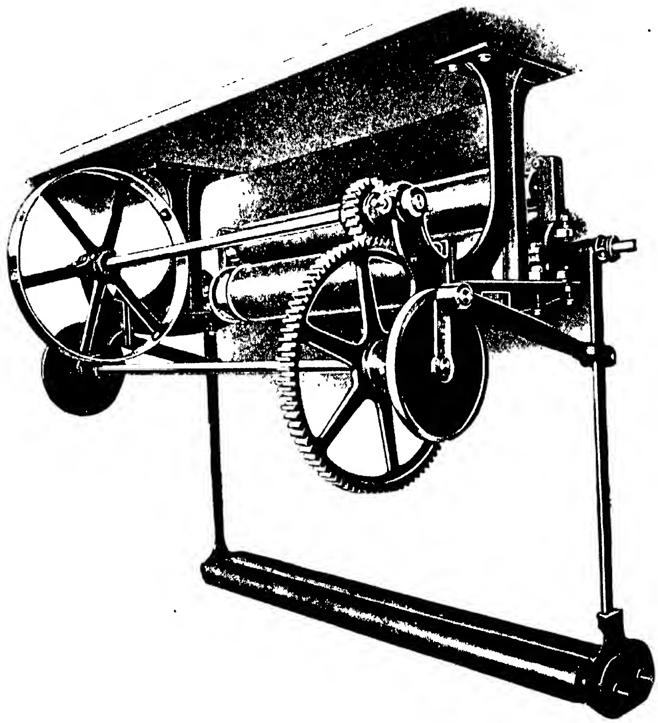


FIG. 260.—Overhead Frilling Folder (Text. Fin. Mchy. Co.).

testing the goods with a solution of potassium iodide and starch paste, which will show a blue or black coloration with chlorine, even in very slight amount.

Oxycellulose is a rather indefinite name given to products obtained from cotton by the action of oxidizing agents and resulting in a tendering of the fiber. Witz has published the results of an extensive and interesting research on the formation and properties of this body. According to him, it is formed by the reaction of nearly all oxidizing agents, such as chlorine, chlorine acids, chromic acids, dilute nitric

acids, alkalies in presence of air, etc., on cotton. By its formation the strength and resistance of the fiber is considerably diminished, especially when the cotton, after oxidation, is treated with alkali or soap; on the other hand the affinity of the cotton for basic coloring matters is considerably increased, while it is lessened for the acid and substantive dyes. The oxycellulose described by Cross and Bevan does not appear to be identical with that of Witz. These former chemists obtained their product by treating cotton on a water-bath with nitric acid of 50 percent strength, washing out, dissolving in alkali, and reprecipitating with acid. The "oxycellulose" thus obtained does not exhibit a greater affinity towards the basic dyes than does ordinary cotton. Another alteration product of cotton, known as "hydrocellulose," is often confused with oxycellulose, from which, however, it appears to differ both in manner of formation and in properties.

Hydrocellulose has been rather comprehensively studied by Girard; it is formed by the action of acids and acid salts on cotton, and does not possess the property of fixing the basic coloring matters. Hydrocellulose is also formed when cotton is boiled with water under pressure. A hydrocellulose can also be produced by the action of strong caustic soda solutions on cotton as in the process of mercerization. Schwalbe regards hydrocellulose as having the formula $6\,C_6H_{10}O_5.H_2O$. The hydrocelluloses are distinguished from oxycellulose in having a much less reducing action on Fehling's solution. Hydrocelluloses formed by the action of non-oxidizing acids have a copper reducing value of 1.9 to 8.8, while that for oxycellulose rises to as high as 34.9. In some cases, such as in the action of acid oxidizing agents, there is doubtless a simultaneous formation of both oxycellulose and hydrocellulose.

Oxycellulose may be developed in cotton during boiling with either caustic soda or lime, and it will form more particularly on those parts of the goods which become dried while still impregnated with the alkali. Hypochlorites may also cause the formation of oxycellulose if the solutions are too concentrated or if employed at too high a temperature or for too prolonged a period. Chloride of lime solutions are more liable to produce oxycellulose than corresponding solutions of sodium hypochlorite, and a further defect in the use of chloride of lime solutions is due to the fact that these liquors are liable to contain small particles of undissolved solid bleaching powder, and when these become lodged in the goods and are allowed to dry therein, oxycellulose may be developed to such an extent as to completely rot the goods at the point of contact, thus causing holes and tender places to appear. In such cases the goods are properly known as being "burnt" in these places.

It has been recently shown that the presence of certain finely divided metals may act as catalytic agents and greatly increase the activity of hypochlorite solutions on cotton. Cotton containing finely ground copper or brass (derived from droppings of lubricating oil on the goods) will become tendered when bleached with hypochlorite liquors. Peroxide of lead (derived from the action of hypochlorite liquor on metallic lead) may also result in the tendering of cotton, es-

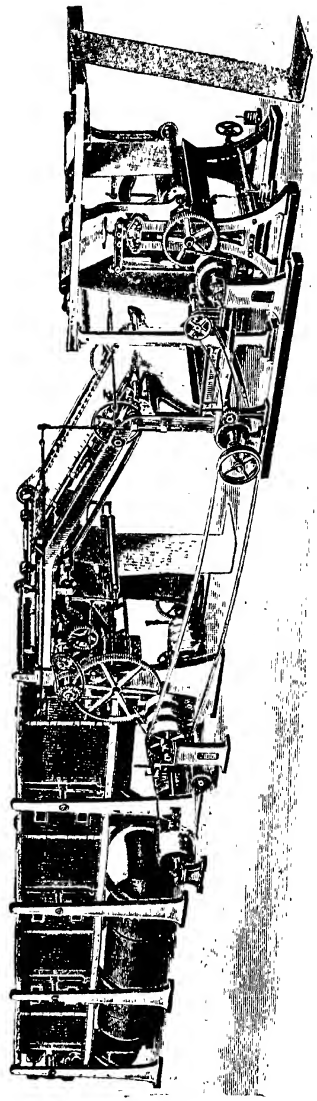


FIG. 261.—Tentering and Drying Machine.

pecially if such goods are subsequently treated to a caustic soda boil.

Oxycellulose may be tested for in bleached cotton goods by staining with a solution of Methylene Blue, a darker color appearing where oxycellulose is present. This test, however, is not very satisfactory, a better one being the test with Fehling's solution, which will give red cuprous oxide, easily detected when in the presence of only traces

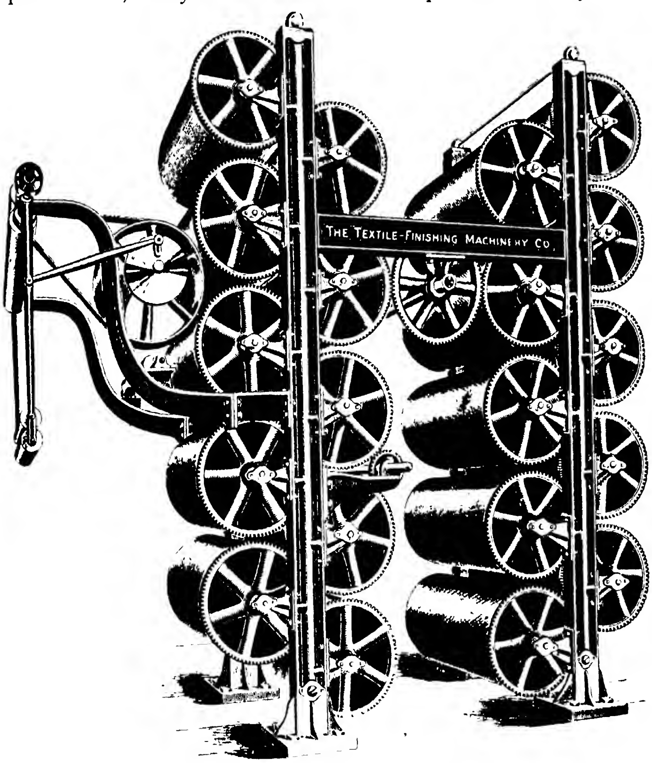


FIG. 262.—Upright Dyeing Machine with Folder (Text. Fin. Mchy. Co.).

of oxycellulose. Oxycellulose dissolves to a yellow liquid when warmed with caustic soda solution. The yellow discolorations which sometimes gradually develop on bleached fabrics are often due to the presence of oxycellulose.

13. **Stains Arising in Storing Bleached Goods.**

Fabrics may turn yellowish on storing at times, and this may be due to imperfect bleaching, whereby the heart of the fiber is not completely bleached, and the only remedy in such a case is to bleach

the goods over again. Or it may be due to over-bleaching, whereby oxycellulose is formed, which in time changes to a yellow color. This fault is without remedy except with injury to the fabrics, as on re-bleaching with chloride of lime this oxycellulose will be disintegrated and the fiber weakened. If the soap is not well removed from the fiber at the end of the bleaching, or if impure and highly colored soap is used, the goods will generally become yellowish in time. Resin soap if used after the treatment with chloride of lime will cause the formation of calcium resinate in the fiber, which at first is white in color, but this gradually turns to a yellow color, hence it is best never to use a resin soap after a chemic.

Oil stains, as already pointed out, are very likely to occur at times on bleached goods, and generally they do not make their appearance until some time after the goods have been bleached and stored. They are usually seen in the form of yellow streaks or spots, and in some cases may be traced to the use of paraffin in the warp sizing. The paraffin wax not being saponifiable is not extracted by the alkalies used in boiling-out the cotton, and when subsequently acted upon by the chlorine of the chloride of lime is converted into chlorine compounds which turn yellow on exposure to the air.

A yellow color may also develop on bleached cotton after storing through the use of improper fats or oils in the dressing or softening materials applied in the sizing or finishing of the goods after bleaching. Tallow, palm and cocoanut oils are extensively used for this purpose. If the fatty matters are not of good quality they may develop rancidity in time, resulting in the formation of a yellowish color on the goods. This defect may usually be detected by a rancid odor in the cotton.

The occurrence of oily threads in bleached goods may give rise to tendering, owing to the fine particles of metal contained in the oil which are usually derived from the bearings of machinery. These threads are usually black in color, and contain finely ground copper or copper oxide. This seems to act catalytically in the bleaching process, resulting in an excessive local oxidation of the fabric, though the full effect of this action may not develop until after the goods have been stored.

Mercuric chloride is sometimes employed as an antiseptic in the starch finish used in sizing yarns. This salt will attack brass rolls (of mangles) and in this way copper may become deposited on the goods. It is therefore recommended that when using metallic salts as antiseptics, salts of the more electropositive elements should be employed.

14. Wood Stains.

When moist cloth (especially if containing soap or alkali) is allowed to remain in contact with wood, as in bins, lattice frames or tables, there is danger of wood stains being formed. Some kinds of wood are more liable to cause stains than others, and on this account careful attention should be paid to the proper selection of the wood to be used in the construction of apparatus for bleaching. Cypress is especially well adapted for this purpose.

15. **Grass Stains.**

Linen material which is bleached by exposure on the grass for long periods of time is very hard to keep free from stains both from the soil and the grass itself. These often require special treatment with soap, oxalic acid or perborate for their removal. Of course this character of stain is not liable to be met with in the modern practice of cotton bleaching.

16. **Testing of Quality of Bleached Cotton.**

It is quite possible by the application of certain chemical tests to ascertain if a fabric has been properly bleached. The more important of these tests may be enumerated as follows:

(a) *Determination of Ash.*—For this purpose 10 grams of the sample are cut up into small pieces and ignited in a weighed crucible until all combustible matter is burned away. In order to obtain a quick and thorough ignition it is well to burn the strips of cloth or yarn by holding them in a forceps in a flame over the crucible. The charred mass of cotton will retain its form and hold together so that it may readily be placed in the crucible for complete ignition. The resulting mineral matter or ash is weighed and its percentage on the weight of the sample calculated. Raw cotton will contain about 1 to 1.3 percent of ash; well boiled-out cotton will give about 0.3 to 0.5 percent of ash, while well bleached cotton will give only 0.02 to 0.15 percent of ash. When bleached with chloride of lime the amount will vary from 0.08 to 0.15 percent, depending on the thoroughness of souring and washing. When soured with hydrochloric acid the ash will be somewhat lower than when sulfuric acid or antichlor is used. Cotton bleached with sodium hypochlorite and properly washed should give only 0.02 to 0.10 percent of ash. If hard water is used for washing a higher percentage of ash is shown than when soft water is employed. If the bleached cotton has been softened or finished with soaps or metallic salts, of course a much higher percentage of ash may be shown than is given above. In such cases the sample should first be well washed in hot water before testing for the ash, as otherwise the results would be misleading. In testing bleached cotton for the ash factor the sample should be taken before any softening or finishing materials have been added, so that the ash may represent only the mineral matter in the bleached fiber itself. The amount of ash thus obtained is a very important indication of the quality of the bleach.[10] If the ash is high (over 0.20 percent) there will be considerable danger of the fabric turning yellow on storing. The cause of this is rather obscure, but is probably due to the presence of lime salts in the fiber acting as a catalyzer in the action of the air on the cellulose of the cotton, resulting in the formation of oxycellulose which shows yellowish stains, and if the action has proceeded to any considerable extent a distinct tendering will also be observed. The

[10] The author has had occasion to examine a very large number of samples of many different kinds of bleached cotton fabrics and yarns where yellowish discolorations developed on storing often accompanied by tendering. In practically every case the yellow and tender parts of the goods showed a much higher proportion of ash than the rest of the material.

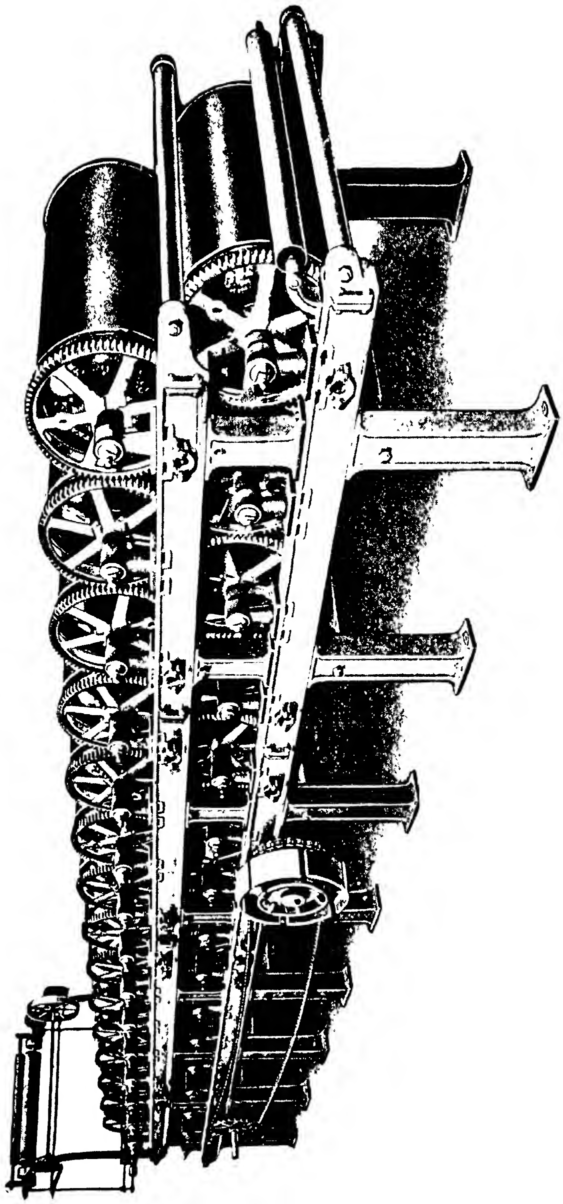


Fig. 263.—Horizontal Drying Cans for Bleached Cloth.

relatively high amount of ash may arise from residues of lime salts left in the goods from the bleaching baths (when using chloride of lime) or from the use of hard water in washing.

(b) *Determination of Oxycellulose.*—As already pointed out oxycellulose may be developed in bleached cotton through excessive oxidation by employing hypochlorite liquors of too great strength, at too high a temperature or for too long a period of time. It may also be formed by improper boiling-out, such, for instance, as kier-boiling the cotton in the presence of air. Furthermore, by allowing acid to dry into the fiber, a hydrocellulose is formed, which for all practical pur-

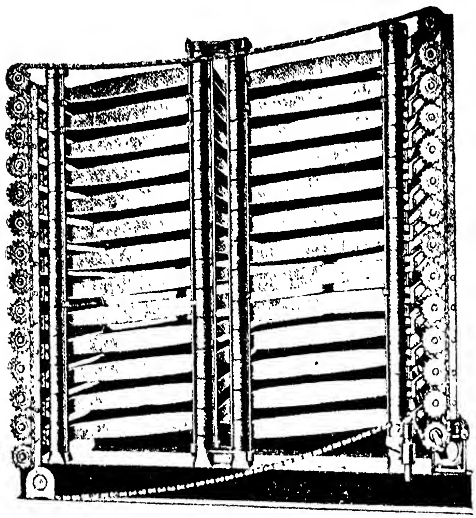


Fig. 264.—Cell Dryer for Cloth (Butterworth).

poses may be considered the same as oxycellulose with respect to the effects on the quality of the bleached goods. The formation of oxycellulose is one of the chief defects to be met with in the bleaching of cotton goods, for if the cellulose of the fiber has suffered any serious degree of alteration into oxycellulose, tendering will invariably result.

In order to test bleached cotton for the presence of oxycellulose, there may be called into use the fact that the latter body has quite an affinity for Methylene Blue, or indeed for basic colors in general, whereas unaltered cotton has not.[11] Another more reliable test has been proposed, which is the property of oxycellulose to reduce Feh-

[11] This test may be carried out by boiling some of the cotton cloth for 5 to 10 minutes in a solution containing 1 part of Methylene Blue in 1000 parts of water and rinsing well. A deep blue tint will develop in places where oxycellulose may be present, whereas the body of the sample will only show a faint tint. This test, however, is not very satisfactory, especially when the formation of oxycellulose is not very strongly marked. The test with Fehling's solution, on the whole, is much to be preferred.

ling's solution. For this purpose, the material to be tested is first treated in such a manner as to remove the substances used in finishing, and is then digested for 15 minutes on a water-bath with a 10

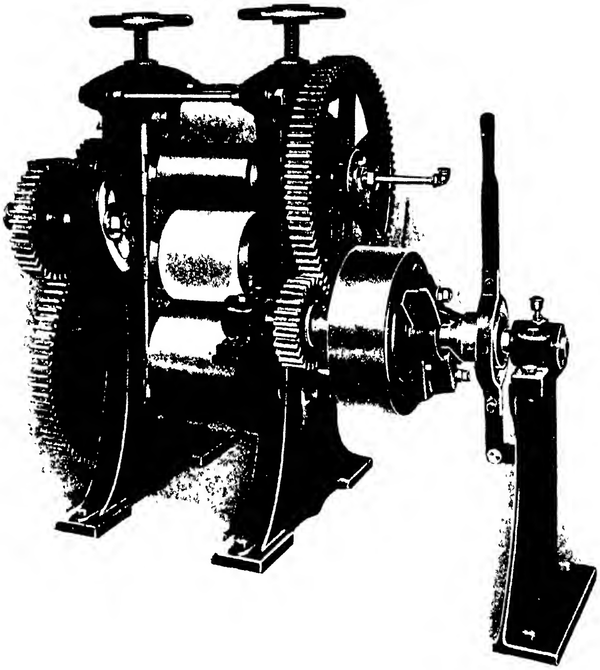


Fig. 265.—Light Friction Calender for Narrow Fabrics (Text. Fin. Mchy. Co.).

percent Fehling's solution,[12] and then well rinsed with water. If oxycellulose is present the fiber will become reddish in color due to the formation of red cuprous oxide. When treated with a solution of fer-

[12] Fehling's solution consists of a mixture of copper sulfate, caustic soda and Rochelle salt. The latter is the compound sodium-potassium tartrate The solution is usually prepared in the following manner: 70 grams of pure crystallized copper sulfate (bluestone) are dissolved in about 200 c c. of distilled water, and if the solution is not perfectly clear a few drops of sulfuric acid are added. There is then added a solution containing 350 grams of Rochelle salt and 100 grams of caustic soda in about 500 c c. of water The mixture is diluted to one liter by the proper addition of water. For each test about 25 c c of this Fehling's solution is used. Owing to the fact that a Fehling's solution prepared in this manner is liable to undergo chemical change and alter in strength, it is frequently made up in the form of two solutions and kept in separate bottles. One solution consists of the copper sulfate dissolved in one liter of water; the second solution consists of the Rochelle salt and caustic soda in the same amount of water. In making the test in this case 25 c c. of each solution is taken and mixed together just previous to use.

The action of Fehling's solution is based on the fact that certain organic bodies, like glucose and certain sugars have the power of reducing the copper compound present in the solution to the form of an insoluble red cuprous oxide. This is one of the characteristic reactions of oxycellulose, and serves to distinguish it from unaltered cellulose, which gives no reaction with Fehling's solution. Hence this method forms a very good means of detecting the presence of oxycellulose, especially as the red cuprous oxide is precipitated in the fiber where the oxycellulose occurs, and becomes fixed therein, thus indicating accurately not only the presence of oxycellulose in a general way, but also just where it occurs.

rous sulfate cotton which has been converted into oxycellulose gives a much heavier shade than with cotton which has been properly bleached; solutions of ferric chloride produce the same effect. Oxycellulose also has a greater affinity for aluminium mordants, which makes itself apparent when the cotton is dyed with Alizarine. Boiling in a 1 percent solution of soda will cause a brown coloration on cotton containing oxycellulose, and the bath also acquires a brownish tint. Steaming of over-oxidized cotton causes it to turn yellow in spots.

(c) *The Copper Index of Bleached Cotton.*—The proportion of oxycellulose present in a sample of bleached cotton may be quantitatively indicated by the determination of what is known as the "copper index" or "copper value." This is done in the following manner (Schwalbe): 3 grams of the sample are reduced to a fine state of division and mixed with 200 c.c. of water and 100 c.c. of Fehling's solution (50 c.c. of each solution). The liquid is boiled for 15 minutes with a reflex condenser with frequent agitation. The liquid is then filtered hot, and the residue containing the red cuprous oxide is washed with boiling water. The cuprous oxide is then dissolved in nitric acid and the amount of copper determined by the electrolytic method. The percentage of metallic copper calculated on the weight of the dry cellulose sample is called the copper index. These values for various cellulose products are given as follows:

Material	Copper Index
Absorbent cotton	1.64
Mercerized bleached Egyptian yarn	1.9
Artificial silk (Glanzstoff)	1.1
Hydrocellulose	5.2
Parchment paper	4.2
Bleached sulfite wood-pulp	3.9
Overbleached sulfite wood-pulp	19.3
Oxycellulose from filter paper and bleaching powder	7.9
Bleached cotton rag pulp	6 5

(d) *Test for Acidity.*—Bleached cotton should also be tested for acidity, especially by the bleacher immediately after the bleaching has been completed. This may be done by boiling a sample of the cloth in water, and adding to the water after cooling a few drops of a solution of blue litmus; if acid is present, the litmus will turn red in color.

(e) *Test for Chlorine.*—The presence of chlorine in bleached goods may be determined by boiling a sample of the cloth in a solution of potassium iodide containing a few drops of starch solution; if free chlorine is present, the solution or the cloth will turn blue.

(f) *Analysis of Bleached Cotton.*—The following method has been suggested for testing the quality of bleached cotton,[13] that is, to ascertain if the bleaching has been properly carried out and in such a manner as to preclude the possibility of the goods turning yellow on storing. The samples, of course, should be taken from the bleached

[13] Well bleached cotton should also conform to the following test: Place a sample of the cloth on the surface of some water contained in a porcelain dish; if the sample is completely and properly bleached it will become wetted out quickly and uniformly, and will sink in the water. This test, however, is only adapted to unsized cloth or yarn and that not containing any softener or oil.

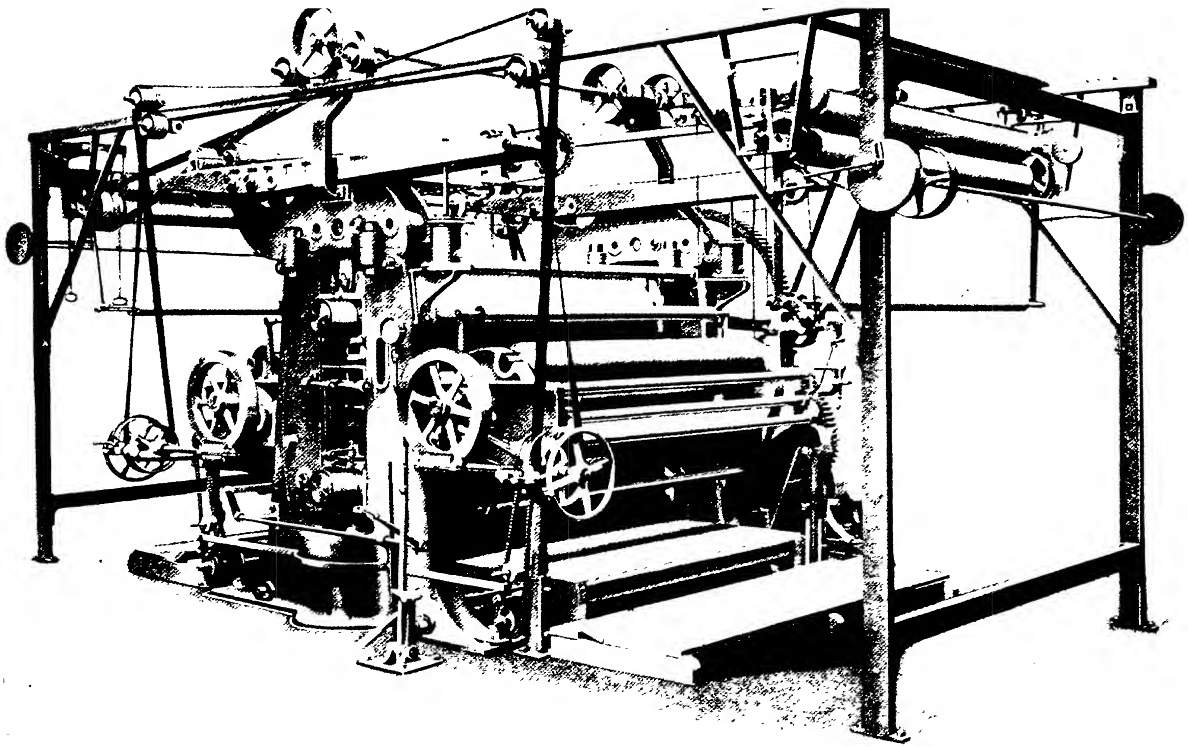


Fig. 266.—Hydraulic Mangle with Two Rollers and Double Revolver for Bleached Goods

fabric before any softening or finishing compounds have been added. There should be a quantitative determination made of: (1) *Free Fat,* by extracting 15 gms. of the material with petroleum ether in a Soxhlet; nearly all fabrics will yield some extract, the amount varying from 1 to 1.5 percent in gray goods, and from 0.01 to 0.008 percent in perfectly bleached fabrics. Bleached goods giving more than 0.04 percent of ether extract should be rejected. (2) *For Lime Soap* (combined fatty acids); the weighed sample which has been extracted with ether is steeped for half an hour in a 5 percent solution of hydrochloric acid, washed well with distilled water, dried, and again extracted with ether in a Soxhlet. The fatty acids thus extracted are dried and weighed; or they may be dissolved in warm alcohol, and titrated with N/20 caustic soda and phenolphthalein. Well bleached cotton will contain 0.03 to 0.04 percent of fatty acids, and materials containing more than 0.08 percent have not been properly soured and washed, while those containing more than 0.12 percent should be rejected. (3) *For Ash;* this is determined in the usual manner by ignition of a weighed sample. Even the best bleached goods will give 0.03 to 0.05 percent of ash. In most cases the amount of ash corresponds to the lime soap present. The following examples are given:

Cloth	Free fatty acid Percent	Fatty acids Percent	Ash Percent
Gray	1.0448	0.1359	1.6294
After boiling with caustic soda and soda ash	0.1761	0.4923	0.2230
Bleached	0.0210	0.0433	0.0571

Besides the chemical tests to be applied to bleached cotton certain physical tests are also of importance, such as tensile strength, elasticity, softness, scroop and quality of color. The tensile strength is perhaps the most important, and this must be determined in comparison with that of the unbleached cotton. In the case of cloth, if the bleaching process has been properly carried out, there should be little or no decrease in the strength of the cotton. In some cases there may even be an increase of strength after bleaching; this is caused by a felting together of the fibers in the cloth, chiefly in the boiling-out process. There is also a shrinkage of the yarns in some cases of bleaching, making a more compact and solid structure, and this will also account for there being no loss in strength. On the other hand, in the running of cotton piece goods in bleaching, there may be considerable tension put on the warp yarns, and this may cause a stretching of the cloth lengthwise and also a loss in strength and elasticity. Higgins has shown that alteration in strength depends largely on the cleanliness of the gray yarn or cloth. If the yarns are well sized and contain much foreign matter, the bleaching process will cause a decrease in strength, but if the yarn is clean and free from sizing there is no such loss.

Chapter XXIV.

Bleaching of Linen.

1. Nature of Impurities in Linen.

Linen differs somewhat from cotton with respect to bleaching in that it contains a greater amount of impurities or substances other than cellulose. Whereas raw cotton contains only 5 percent of foreign matters, linen contains about 25 to 30 percent.[1] These substances are chiefly composed of waxy and pectin matters resembling, no doubt in a general manner, those existing in cotton. It is, however, also encrusted with more or less intercellular matters which differ in composition and properties from the impurities in cotton. Whereas cotton consists mainly of pure cellulose, flax or linen contains relatively large quantities of certain alteration products of cellulose, particularly *pectocellulose*. The latter may be considered as a compound of cellulose with pectose, a widely distributed vegetable constituent. Pectose, up to the present time, has not been isolated in a free state; it is insoluble in water, alcohol, and ether, but through the simultaneous action of acids and heat it furnishes a body soluble in water, and known as pectin. The latter is converted by the action of alkalies into an insoluble body possessing acid properties known as pectic acid. Also under the influence of special ferments, pectose is converted into soluble products. The salts of pectic acid (the pectates) have never been isolated in a pure condition and little is actually known concerning them. There are other compounds of cellulose also present in the flax fiber, to which the names *adipocellulose* and *cutocellulose* have been given, and it is to the presence of these compounds that the chief difficulties attached to the bleaching of flax is attributed. Cutocellulose is a substance which appears to form the chief constituent of cork, or the exter-

[1] Strutt relates the following concerning the bleaching of linen in the Middle Ages: "When they had completed their linen in the loom they proceeded to use several arts to make it more beautiful and soft and to bleach it; the whole process as well as the whitening of the flax before it went to the loom was as follows: The spun yarn was put into a mortar, where it was pounded and beaten in water; when it was come to a certain whiteness it was sent to the weaver, and when it was received again from him made into cloth, it was laid upon a large smooth stone and well beaten with broad-headed cudgels; the more frequently it was beaten and the more labor was bestowed, the softer and whiter the cloth always proved, but very frequently they would mingle the juice of poppies with the water which they used on these occasions, and it was thought to contribute considerably to making the linen more white and beautiful. Sometimes they used soap to scour their cloths, which soap they made from the fat of animals and the ashes of certain vegetables."

The earliest work written in English on the subject of bleaching was perhaps that of Francis Home in 1756 describing the practice of bleaching linen in the Netherlands and in Ireland.

In the middle of the seventeenth century Dr Home of Edinburgh suggested the use of water acidulated with sulfuric acid in the bleaching of linen in place of buttermilk or sour milk. Dr. James Ferguson of Belfast received recognition from the Irish Linen Board for the successful application of lime in bleaching.

nal coating of plant tissues. Adipocellulose is a wax or fatty-like substance, and as a constituent of the flax fiber it appears to play an important part in the spinning operations, imparting suppleness and resiliency to the fiber. Various facts seem to indicate that the composition of the adipocellulose matter in any variety of flax is a generic characteristic of the same, and chemically speaking, the varieties of the fiber differ solely in respect to the nature of their adipocellulose. According to the analyses of Hodges and Cross, retted flax contains

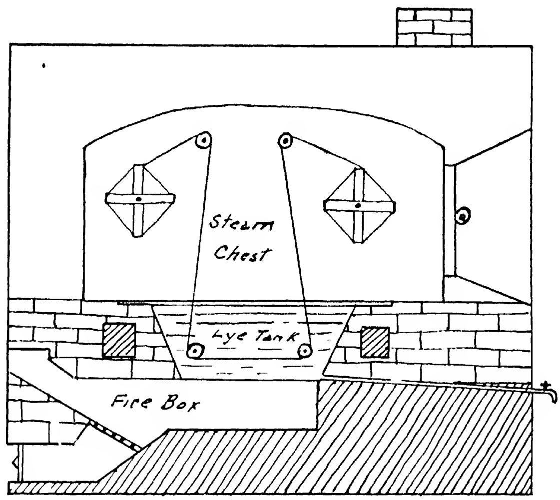


FIG. 267.—Early Method of Linen Boiling.

about 3 to 4 percent of adipocelluloses; and in this connection it may be said that the following constituents are to be found in flax:

Substance	Percent
Pure cellulose	65 to 70
Pectic substances	20 to 25
Woody and cuticular tissue	4 to 5
Ash	1

Linen is more easily affected by alkalies, acids, and hypochlorites than cotton; in consequence of which more care must be taken in its bleaching in order to preserve the good qualities of the fiber intact. In its general outline the process of bleaching linen is very similar to that for cotton, only weaker solutions are employed and a longer time is required. It also appears essential for the proper bleaching of linen to expose it on a meadow to the action of the sun and dew, generally known as "grassing." The effects produced by grassing are no doubt due to the action of ozone or hydrogen peroxide liberated by the sun slowly evaporating the dew in the cloth. Again linen has much more coloring matter in it than cotton, and these pigments are probably of a

different nature than the ones present in cotton; consequently there are several grades of linen bleaching, called full, three-quarter, half, or one-quarter, according to whether all of the color is taken away or only a portion of it. In a full bleach, the linen fiber is always more or less weakened.

According to the experiments of Kolb, the pectin matters in the linen fiber are converted into meta-pectic acid when boiled with lime, and this meta-pectic acid then passes into solution. For every 100 parts so dissolved, 48 parts of lime pass into solution. Linen boiled

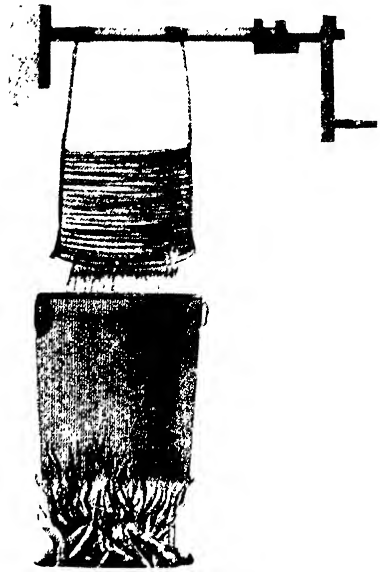


FIG. 268.—Primitive Form of Kier for Boiling Linen.

with soda ash alone is usually softer than that boiled with caustic soda, which is accounted for by the fact that the former alkali dissolves less of the fatty matters which are present in the fiber. Linen boiled in lime and caustic soda solutions loses from 15 to 30 percent in weight, depending upon the character of the fiber. Bleaching powder solutions appear to remove very little pectic acid from the fiber; and in fact, the latter apparently prevents the chloride of lime from destroying the gray coloring matters in the fiber and becomes fixed itself. Hence, the majority of the brown matters (the pectin substances) should be completely removed in the boiling-out, otherwise they will not be completely removed in the bleaching.[2]

2. Boiling-out of Linen.

The removal of impurities from linen goods previous to bleaching this fiber is accomplished in much the same manner as employed in

the case of cotton. The linen is boiled-out in an open or a closed low-pressure kier with an alkaline liquor. Milk of lime, soda ash or caustic soda may be used as the alkaline agents. The kier should be provided with an efficient device for circulating the liquors through the goods and practically the same kind of apparatus is employed as in the case of cotton.

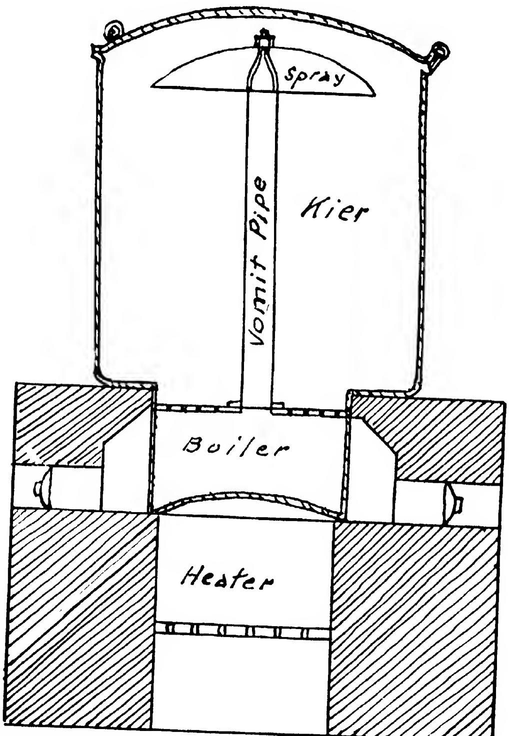


FIG. 269.—Kreisig's Process for Boiling-out Linen (1834).

As linen contains a much greater proportion of impurities than cotton, in order to obtain a good clear white color in bleaching it is necessary to prepare the material by a very thorough preliminary treatment or boil-out, for a satisfactory bleach cannot be obtained until the impurities are completely removed. It is also to be borne in mind that linen is a harder fiber than cotton and is not so easily penetrated, especially in the form of a woven fabric. On the other hand, it is also important to remember that the long commercial linen fiber is in reality

[2] Well bleached linen should not be discolored when steeped in a 10 percent solution of ammonia. If the linen shows a yellow coloration as a result of this treatment it indicates that the waxy and pectin matters have not been properly removed.

composed of a number of comparatively small cell elements held together by a cementing intercellular tissue (in common with all bast fibers) and if severe chemical treatments are given to the fiber there is grave danger of breaking down the main fiber into its minor con-

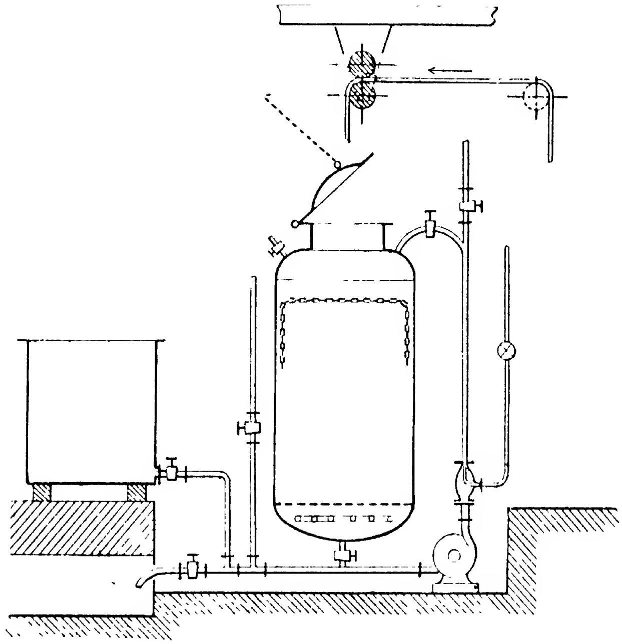


FIG. 270.—Early Pump Kier for Linen Boiling.

stituents, thus leading to a weakening or disintegration of the fabric or thread. It is necessary therefore to avoid too severe a treatment in the boiling-out of linen or the use of too strong chemicals in the bleaching. On this account the proper and efficient bleaching of linen is a somewhat more tedious and complicated process than the bleaching of cotton.[3]

[3] The boiling-out of flax or linen is somewhat similar to that process as used for cotton, although owing to the difference in the nature and amounts of impurities present on these two raw fibers there is some difference in the results obtained. The pectin matters on flax yarns is rendered soluble by prolonged boiling in water alone, but the process is much more rapidly carried out if alkaline solutions are used. Owing to the composite structure of the flax fiber as compared with that of cotton, it is natural to expect that the boiling-out would bring about a certain amount of weakening, due to a loosening up of the intercellular cementing tissue holding the small fiber elements together to form the long linen fiber. A study on this subject was made a number of years ago by Kolb, who, however, worked only with small laboratory samples and not under the practical conditions of mill operation. His conclusions were that (a) the weakening of the fiber was not proportional to the loss in weight due to the boiling-out; (b) the concentration of the caustic soda solution used in the boiling-out had but little influence on the loss in strength of the fiber; (c) caustic soda was more liable to cause weakening than soda ash; (d) milk of lime even in the cold produced a weakening effect; (e) the greatest danger in the boiling-out as far as the weakening of the fiber is concerned is a result of a too prolonged boiling, which under no circumstances should exceed a period of eight hours

In order to remove the large amount of impurities present in linen it is customary to employ a series of repeated treatments with alkaline liquors alternating with sours (dilute acid solutions) and thorough washings. These operations must be conducted with care and skill if the full quality of the linen is to be preserved.

The more thoroughly linen is boiled-out and the whiter it is bleached the weaker does the fiber become and the less durable the fabric. For the production of ordinary creamed linen it is sometimes

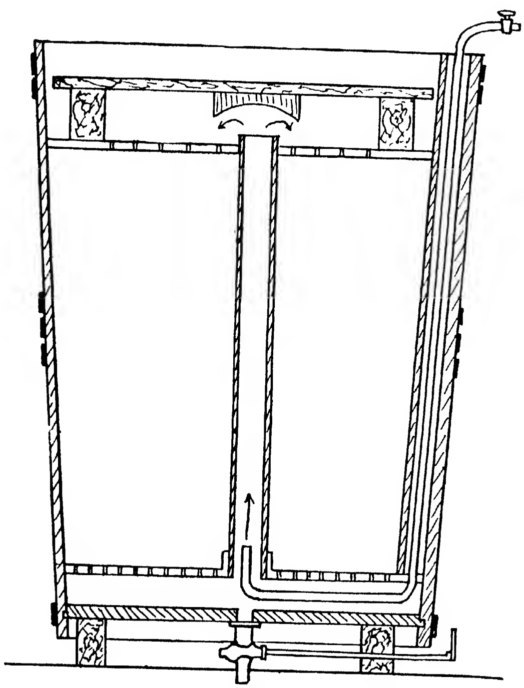


FIG. 271.—Open Kier with Injector for Boiling Linen.

necessary only to give the material a good boil-out and sour, without the use of any bleaching agent proper (such as hypochlorite liquor). For a good satisfactory white, however, a further complete bleaching treatment is necessary.

In all the treatments of linen it must be remembered that the fiber is more easily affected by alkalies, acids and bleaching agents than cotton, and consequently there is always more danger of tendering the goods. Another reason for the avoidance of too severe a treatment in the boiling-out of linen is the danger of "setting" the color; that is to say, causing a discoloration of the linen through an improper decomposition of the natural impurities of the raw fiber. The result will

be that colored resinous bodies are produced which prove to be exceedingly difficult to remove or bleach out. This fault in boiling-out is one which is very difficult to deal with, and frequently results in the production of ruined fabrics or seconds of little value. It is well on this account to avoid the use of too high a temperature in boiling-out and the use of too strong alkaline liquors.

It is also important to preserve as far as possible the luster of the linen fiber when subjecting it to the various bleaching operations, for it is on the luster to a considerable extent that the high and valuable quality of linen depends, and if this is lost the value of the material is much depreciated. The bleacher considers loss of luster as being due to the "skin of the fiber being broken." On this account it is always well to use as weak solutions of chemicals as expedient in the treatment of linen, repeating the operations of treatment a number of times if necessary to obtain the desired action rather than using more concentrated solutions.

3. Bleaching with Chloride of Lime.

As with cotton, the principal method of bleaching linen is a treatment with a solution of hypochlorite. Chloride of lime is the chief agent used in this case, though of recent years the use of sodium hypochlorite is coming more and more into favor, especially since the introduction of liquefied chlorine for the preparation of sodium hypochlorite bleach liquors. In the use of chloride of lime liquors for the bleaching of linen rather weak solutions are employed, considerably weaker, as a rule, than when bleaching cotton. While in the latter case it is customary to use bleaching powder solutions standing at 1½° to 2½° Tw., in the case of linen bleaching the solutions generally employed range from ½° to 1½° Tw. The use of stronger solutions is to be avoided, as the fiber is liable to be decomposed into its cell elements with a consequent weakening of the fabric.

In the use of chloride of lime care must also be had to avoid the occurrence of residues of the chemical in the bleached fiber, as the presence of either chlorine or lime compounds will in time cause a deterioration of the linen. The coloring matter to be bleached from linen is quite different both in character and amount from that in cotton. Not only is the coloring matter of the cell elements to be considered, but also the color in the cementing tissues between the cell elements must be reckoned with. In both cases hypochlorite solutions appear to be efficient bleaching agents, and the treatments with the solutions of chloride of lime may be so carried out as to cause but little tendering of the fiber by breaking down of the connecting tissue cementing together the cell elements.

4. Bleaching Linen Yarn.

The bleaching of linen yarn is essentially very similar to that of cotton, the general treatments being kier-boiling in soda, chemicking with hypochlorite (of either soda or lime), souring with sulfuric acid and thorough washing. Linen yarn is seldom bleached to a full white,

but is simply "creamed" or about half bleached. Hummell gives the following method:

(1) Boil 3 to 4 hours with 10 percent soda ash; wash and squeeze.
(2) Reel for 1 hour through bleaching powder solution of ½° Tw.; wash.
(3) Steep 1 hour in sulfuric acid at 1° Tw.; wash.
(4) Boil 1 hour in 2 to 5 percent soda ash; wash.
(5) Repeat number 2.
(6) Sour again as in number 3; wash well.[4]

This process should yield a half-white yarn. If a three-quarters bleach is required, operations 4, 5, and 6 are repeated, only that after the second boil the goods are spread out on the grass for about a week, and instead of reeling the yarn through the bleach liquor it is simply

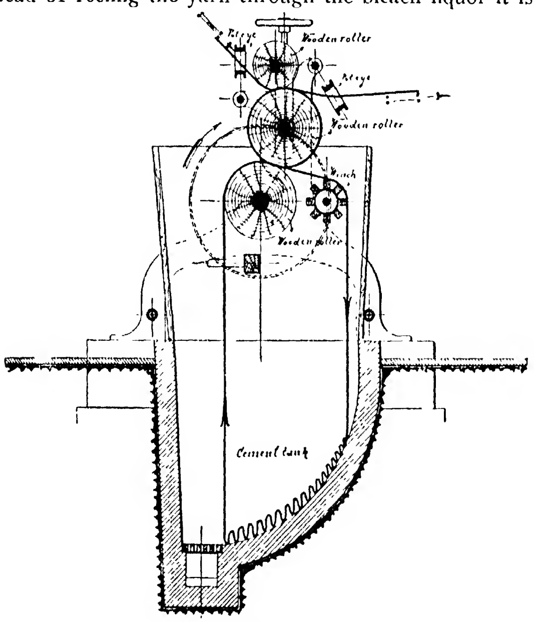


FIG. 272—Machine for Chemicking and Souring Linen Cloth.

steeped therein for 10 to 12 hours; which operation is usually called the "dip." Should a full bleach be required the operations are repeated several times, and the duration of grassing lengthened. The boiling-out in soda is best done in a low pressure kier, and the souring and washing and chemicking are done in machines or tanks similar to those employed for cotton.[5] It is better to use sodium hypochlorite

[4] In linen bleaching 1 pound of yarn will require about 25 gallons of water for washing after each operation of boiling, chemicking and souring.

[5] It is interesting to examine the appearance of the yarn after each operation; the shade acquired after the first lye-boil in particular, affords a good idea of the difficulty which will be encountered in bleaching the yarn. For example, a yarn that has turned deep blackish gray (dew-retted flax) in color will generally bleach better than one that shows a reddish

for chemicking than chloride of lime, as the lime compounds are apt to harden the fiber. It is also said that magnesium bleach liquors are very good in this respect. The use of hydrochloric acid instead of sulfuric is also to be recommended for the same reason. For chemicking the goods it is best to employ what is known as a reeling machine. This consists of a shallow trough of cement, wood, or masonry over which is placed a series of small wooden rollers on which the hanks of linen yarn are hung, and from which they hang into the solution of chloride of lime. These reels receive an alternating backward and forward motion so that the hanks are circulated through the solution and also exposed to the air. The exposure to the air results in the action of the carbonic acid on the chloride of lime so that hypochlorous acid is liberated in the fiber and the bleaching so proceeds.[6]

The souring and washing may also be carried out on the reeling machine.

In America the grassing operation is never resorted to in the bleaching of linen yarns, the hypochlorite bleaching alone being relied upon. Attempts have also been made to use the permanganate bleach in connection with the hypochlorite process, but this so injures the strength of the fiber that it is not practical.

Linen yarns will lose from 10 to 20 percent in weight, depending on the extent of the bleaching; and the principal decrease in weight occurs when boiling in alkali.

Tailfer recommends the following strength of chloride of lime solutions for different sizes of linen yarns:

No. 10 to No. 20	3°	chlorometric strength
20 to 35	2°	" "
35 to 45	1.5°	" "
45 and upwards	1°	" "

According to Ganswindt, linen may be bleached in a day by the use of solutions of potassium permanganate and sodium bisulfite, operating as when bleaching cotton.

A method for the bleaching of linen yarn much in use at the present time is the following: The yarn is first soaked over night in a weak solution of caustic soda and soap, which softens up the fiber and has considerable influence on the resulting operations. The material is then placed in a kier and boiled from five to six hours at a pressure of two atmospheres in a solution containing 4.5 lbs. of soda ash and 1 gallon of caustic soda (76° Tw.) for each 100 lbs. of yarn.

cast; not that the former bleaches more rapidly, but that it gives a better white finally with the same number of operations. After the first chemicking, the color of the yarn will usually be lighter, and pale yellow; after again boiling in lye, the shade again changes to brown; the treatment with alkalies modifying the pectic substances oxidized by the chlorine, and converting them into colored soluble meta pectates.

[6] In the chemicking of linen and hemp yarns the operation is usually carried out in cement tanks about 20 inches deep, in which the banks are suspended vertically. This is frequently done in such a manner that the skeins do not dip entirely into the liquor and are caused to rotate on a movable reel so that they are alternately exposed to the bleach liquor and to the air This operation is known as "reeling" the yarn in the bath. The exposure of the material saturated with the chemic solution to the air brings into action the atmospheric carbon dioxide which very materially facilitates the bleaching. The reeling process of bleaching is applicable to rather coarse yarns, but is not suitable for finer yarns as the exposure to the air is liable to cause weakening of the fiber, and the reeling motion has a tendency to roughen the threads or tangle the skein.

After boiling the required length of time, the liquor is run off, and then cold water is run in until the washings are clear. The yarn is now given a second boil which consists of the same operation as the first boil, only the solution contains 2 percent of soda ash and 2 percent of caustic soda, and the boiling is continued five hours. A thorough washing is next given the goods, after which they are boiled a third time for five to six hours under similar conditions to the second boil. After draining and washing, the yarn is next placed in a solution of

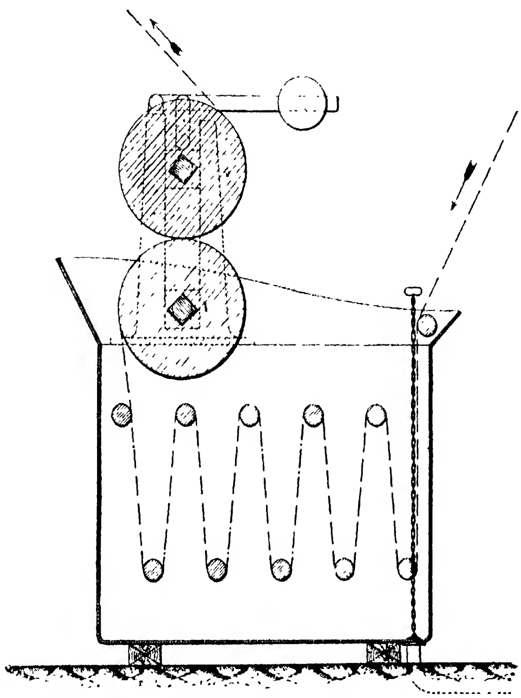


FIG. 273.—Saturating Machine for Liming Linen Cloth.

bleaching powder of 3° Tw. strength. The solution should be freshly prepared and should not contain any undissolved particles of lime. The yarn is steeped in this chemicking solution for 2 hours, then rinsed, and soured in a bath of sulfuric acid at ½° Tw. for ½ hour. After this, it is well washed and then boiled in a weak soap bath, and washed again. The yarn is then given two further treatments with the bleaching powder solution, each for one hour. It is finally washed, soured, and again washed, and then tinted with Ultramarine.

In the bleaching of linen yarn it is said that the strength of the

fiber is better preserved if an electrolytic bleach liquor or one of sodium hypochlorite is employed. If an electro-bleach liquor is not available it is recommended to use for the bleaching bath a liquor prepared as follows: 60 lbs. of bleaching powder are mixed with water, and then made up to 25 gallons; a solution is next made of 35 lbs. of soda ash in 13 gallons of boiling water, then 6 gallons of cold water are added, and the solution is mixed with that of the bleaching powder, and allowed to stand overnight. The clear liquor is drawn off, and the residue is washed four times with cold water, and the whole liquor is made up to 125 gallons with cold water, or so that it will

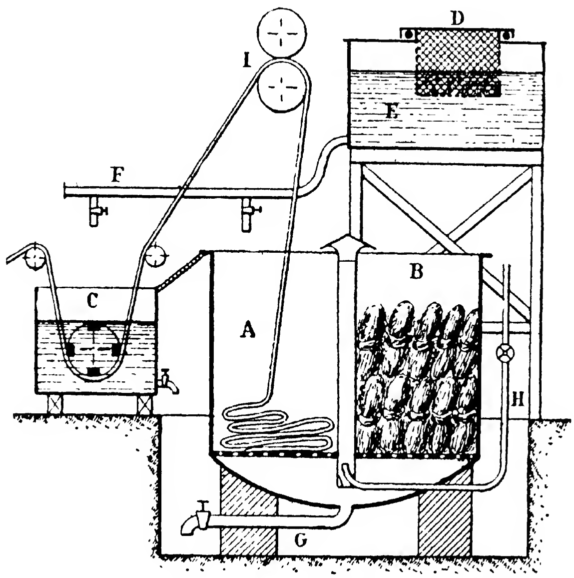


FIG. 274—Early Type of Lime Kier for Linen Goods.

stand 6° Tw. As the liquor still contains some lime, from 1 to 2 lbs. of soda ash are added to precipitate the rest of the lime as calcium carbonate. The solution will now be alkaline and may be neutralized by adding a small quantity of sulfuric acid (about ½ pint of the acid to 100 gallons of liquor).

Some bleachers consider that hot alkaline liquors have a tendency to seriously tender the linen fiber, and they consequently substitute for the alkaline bath one of dilute sulfuric or hydrochloric acids, this being followed up by bleaching with sodium hypochlorite. The process is used especially for yarn, the hanks being strung on sticks and steeped for 5 to 10 minutes in a bath of sulfuric acid at ½° Bé., then rinsed, drained and bleached with sodium hypochlorite at 2° Bé., until

a cream-white color is obtained. The yarn is then rinsed and drained and steeped in a bath of sulfuric acid at ¼° Bé., and then aired and dried. If hydrochloric acid is substituted the same degrees of concentration should be used. Two baths of sulfuric acid should give a cream-white; a bath of hydrochloric followed by one of sulfuric acid gives a half-white; and two baths of hydrochloric acid give a yellow-cream. These tints may be fixed by passing the linen through a bath of soda ash. It is said that these processes yield a thread remarkable for brilliancy and suppleness without weakening. The final washing must be very thorough in order to remove all traces of acid from the fiber.

Ledebur gives the following table showing the loss in weight on bleaching different counts of linen yarn:

	Yarn Number					
Degree of Bleach	6	10	20	30	40	60
¼	25.%	23.%	21 5%	20.%	19.7%	18.%
½	27.	25.	23.	21.5	20.5	19.5
¾	29.	26.5	24.5	23.	22.	21.
Full	31.	28.	26.	24.	23.	22.

Lowenthal, however, considers these figures somewhat high, and gives the loss for ½, ¾ and full bleach as 15, 18, and 20 percent respectively.

5. Bleaching Linen Cloth.

This is carried out in the same general manner as when bleaching cotton cloth, only linen is also usually exposed to the grassing operation, and also a previous steeping operation before boiling-out is often used. Hummell gives the following process for bleaching linen by the Irish method, on a basis of 1,500 kilos. of material:

(1) Boil for 14 hours with 125 kilos. lime; wash 40 minutes in the stocks.

(2) Sour with hydrochloric acid of 2½° Tw., steeping 2 to 6 hours; wash 40 minutes in the stocks.

(3) Give first lye boil for 8 to 10 hours with 30 kilos. caustic soda and 30 kilos. rosin previously dissolved and boiled together in water. Run off liquor and add second lye boil of 15 kilos. caustic soda; boil 6 to 7 hours; wash 40 minutes in the stocks.

(4) Expose for 2 to 7 days on the grass according to the weather.

(5) Chemic with chloride of lime at ½° Tw., steeping 4 to 6 hours; wash 40 minutes in the stocks.

(6) Sour with sulfuric acid at 1° Tw., steeping 2 to 3 hours; wash 40 minutes in the stocks.

(7) Scald with 8 to 13 kilos. caustic soda, boiling for 4 to 5 hours; wash 49 minutes in the stocks.

(8) Expose on grass for 2 to 4 days.

(9) Chemic in chloride of lime at ¼° Tw., steeping for 3 to 5 hours; wash 40 minutes in the stocks.

The goods are now sorted and those which are sufficiently bleached are taken out; the others are treated further:

(10) Wash on rubbing boards with a strong solution of soft soap.

(11) Expose on grass for 2 to 4 days.

fiber is better preserved if an electrolytic bleach liquor or one of sodium hypochlorite is employed. If an electro-bleach liquor is not available it is recommended to use for the bleaching bath a liquor prepared as follows: 60 lbs. of bleaching powder are mixed with water, and then made up to 25 gallons; a solution is next made of 35 lbs. of soda ash in 13 gallons of boiling water, then 6 gallons of cold water are added, and the solution is mixed with that of the bleaching powder, and allowed to stand overnight. The clear liquor is drawn off, and the residue is washed four times with cold water, and the whole liquor is made up to 125 gallons with cold water, or so that it will

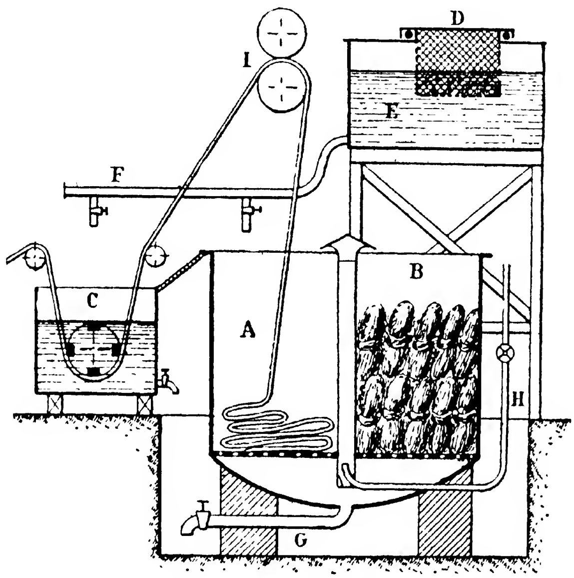


FIG. 274—Early Type of Lime Kier for Linen Goods.

stand 6° Tw. As the liquor still contains some lime, from 1 to 2 lbs. of soda ash are added to precipitate the rest of the lime as calcium carbonate. The solution will now be alkaline and may be neutralized by adding a small quantity of sulfuric acid (about ½ pint of the acid to 100 gallons of liquor).

Some bleachers consider that hot alkaline liquors have a tendency to seriously tender the linen fiber, and they consequently substitute for the alkaline bath one of dilute sulfuric or hydrochloric acids, this being followed up by bleaching with sodium hypochlorite. The process is used especially for yarn, the hanks being strung on sticks and steeped for 5 to 10 minutes in a bath of sulfuric acid at ½° Bé., then rinsed, drained and bleached with sodium hypochlorite at 2° Bé., until

in the same manner as with cotton, and then placed in kiers and boiled for eight hours under high pressure, or for fourteen hours under low pressure.

(3) *Souring.* This is for the purpose of dissolving out the lime compounds, and is done by passing the cloth through a dilute solution of hydrochloric acid.

(4) *Second washing.* This is done with soda and rosin for the purpose of removing the fatty acids liberated in the preceding reaction; 35 parts of caustic soda and 20 parts of rosin are used. The pieces are boiled for about 8 hours, then washed in hot water and finally in cold.

(5) *Grassing.* The grass on which the pieces are spread should be high and sufficiently strong to prevent the cloth from coming in contact with the soil, which would lead to a rapid destruction of the material. If the grass does not fulfill these conditions, it will be necessary to stretch horizontal ropes to support the pieces. Dew and snow are favorable to the process, which ordinarily requires from 7 to 5 days.

(6) *Chemicking.* This is done by allowing the pieces to steep for 6 hours in a solution of chloride of lime at 1° Tw.

(7) *Second souring.* This is effected in a bath of hydrochloric acid at 1½° Tw, in which the material is steeped for three hours, after which it is washed thoroughly.

(8) *Third scouring.* This is done with 8 to 13 parts of caustic soda, and requires about 6 hours.

(9) *Second grassing.* This is carried out in the same manner as the first, but lasts only from 2 to 4 days.

(10) *Second chemicking* This is to terminate the bleaching, and is done with a chloride of lime bath at 1° Tw. This treatment is followed by a thorough washing.

(11) *Final acid treatment* This is to destroy the last trace of hypochlorites, which would otherwise be left in the pieces in spite of the most thorough washing. A final rinsing with a large amount of water finishes the treatment. The loss in weight in linen bleaching by these operations amounts to about 36 percent, and good linen bleaching requires from 4 to 6 weeks' time to complete.

Ganswindt gives the following process for linen bleaching as practiced in Silesia. The pieces are trodden down evenly in a large wooden tub with pure water heated to 95° F. After the tub is filled it is covered over and left that a fermentation may set in, which lasts about 36 hours. After this the goods are taken out, rinsed, and grassed for 2 to 3 days. This steeping process causes the linen to lose about 10 to 15 percent in weight. A first lye boil is now given in low pressure kiers with a 1 percent of soda ash, after which they are grassed again for 2 to 3 days. A second lye boil is then given, followed by another grassing, and these two operations are repeated for about 8 times, each time decreasing the strength of the lye boils. The goods are now rinsed and soured for 5 to 8 hours in sulfuric acid at 1° Tw., and then well washed. Next they are chemicked with chloride of lime for 6 to 8 hours at ½° Tw. A second sour is then given similar to the first; after which the pieces are well washed and treated with a soap solution at 90° F., then they are grassed for 2 to 3 days. The goods are then passed through the rubbing boards, and then treated with a warm soda solution (1 part soda to 400 parts water). They are grassed again for 1 day, washed and chemicked the second time with chloride of lime like the first. Wash and sour as before; then soap again, and grass for 2 to 3 days.

Herzfeld gives the following Irish process without grassing:[7]

(1) Steep for 36 hours in a solution of soda ash at 1° Tw.; wash.

(2) Boil for 6 to 10 hours 3 parts caustic soda per 400 parts water; or use a solution of rosin soap containing 3 parts rosin and 3 parts caustic soda per 200 parts water.

(3) Chemic for 10 to 15 hours with chloride of lime at ½° Tw.; wash.

(4) Sour for 3 to 6 hours in sulfuric or hydrochloric acid at ½° Tw.; wash.

(5) Give second lye boil with ½ part caustic soda per 100 parts water for 4 to 5 hours; wash.

(6) Chemic again in chloride of lime at ¼° Tw., steeping for 10 to 14 hours.

(7) Sour as in 4.

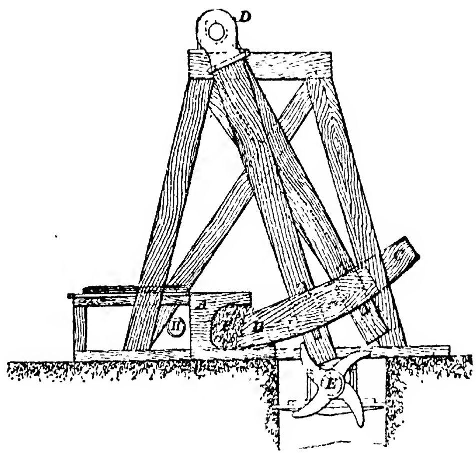


FIG. 276.—Diagram Showing Action of Wash Stocks.

The goods are now sorted and those not sufficiently bleached are further treated as follows:

(8) Pass through the rubbing boards with a strong solution of soft soap.

(9) Chemic with chloride of lime at ¼° Tw.

(10) Sour as before; wash; tint; and finish.

An authority on the Irish linen trade thus describes the modern method of bleaching linen in Ireland: About 140 pieces of yard wide brown linen, each one marked with a red thread, are stitched together

[7] A modern Irish process of bleaching linen yarn is given as follows:

(1) Boil-out with 10 percent soda ash (either a low-pressure or high-pressure kier may be used); wash and squeeze.

(2) Chemic for 1 hour with chloride of lime liquor at 1° Tw.; wash well.

(3) Sour with ½ percent solution of sulfuric or hydrochloric acid; wash well.

(4) Chemic a second time; wash.

(5) Sour a second time; wash and dry. This will furnish a good half-bleach. A three-quarter bleach is obtained by boiling a second time with soda ash; then grass bleach for 1 week; chemic again with weaker solutions of chloride of lime, wash, and sour. By repeating these operations several times a full bleach is produced.

end to end in one piece amounting to about 10,000 yards; this is called a "pot." It is first passed through a solution of lime into the boiling pot and there boiled for 8 to 10 hours. It is then drawn through a tank of water. The pieces are then washed and each one bundled separately.

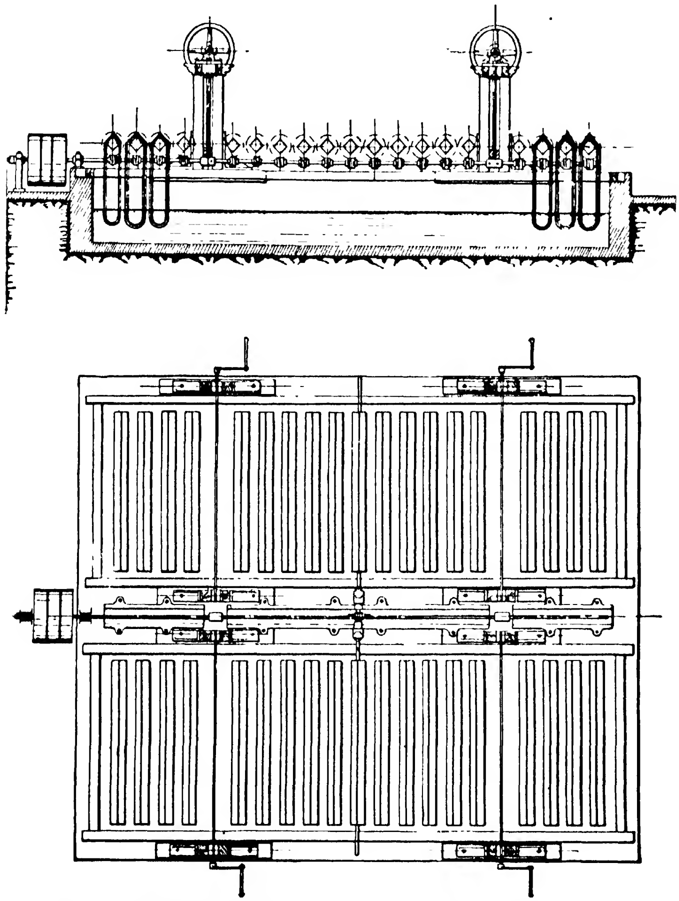


FIG. 277.—Bleaching Machine (Reel) for Linen Skein Yarns.

The cloth is washed in the wash mill with pure water for 1 hour, and then steeped in a sour of dilute hydrochloric acid to convert the residue of lime into soluble salts, then washed again in the mills, then boiled in soda lye. The cloth is next washed again and grassed, rubbed in soap and water, boiled in lye, washed again, grassed and the operations repeated until the desired degree of bleach is obtained. As soon as the

cloth has been sufficiently boiled, the whitening process is begun by the use of bleaching powder or "dip" in which the cloth is left overnight. It is then washed, heated with dilute sulfuric acid, boiled again with soda lye, and the processes repeated as desired in order to obtain the required results.

In the bleaching of linen it would seem that the old form of grass bleaching is still adhered to to some extent, though in practically all linen bleaching at the present time solutions of chloride of lime and sours of sulfuric acid are employed as necessary adjuncts to the grassing of the cloth or yarn. The old-fashioned bleacher claims that proper linen bleaching cannot be obtained by the more modern methods of chemical treatment in which the grassing process is eliminated entirely; it is supposed that the fiber is rotted and its quality is spoiled

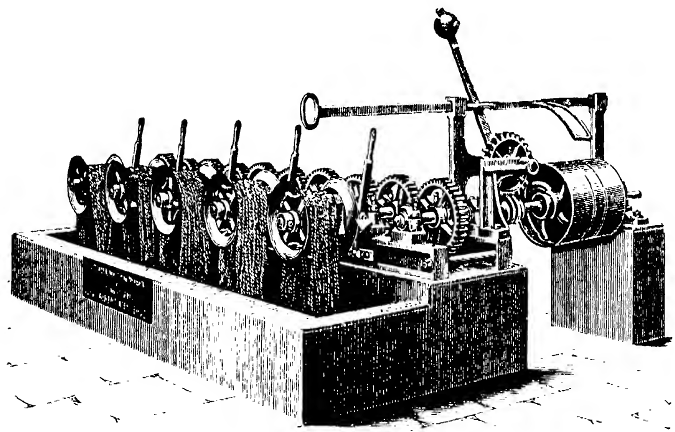


Fig. 278.—Reel Machine for Scouring and Chemicking Linen Yarns.

by the use of chemical compounds. We believe, however, that a good deal of this is traditional buncombe, and if the matter were properly studied so as to obtain the necessary data to describe the required conditions to be met in the bleaching of linen it would be perfectly possible to evolve a process which would take the place of the old-fashioned grass bleach and yet yield a product the equal in every way to this method. From the very fact that even the old-fashioned linen bleacher at the present time employs hypochlorites and sours in his process is a confession on his part that the grassing of the cloth is not capable of producing the best results. To obtain a high degree of white by the grassing process alone would necessitate the exposure of the material to the atmospheric agencies for so long a period of time that the chances are the cloth would be ruined in more ways than one. Stains, dirt, tears due to wind, rotting of the fiber and a hundred other different troubles would arise. Immense tracts of land would

have to be set aside for bleaching greens, the grass would have to be cultivated particularly, there would have to be isolation from railroads, other manufacturing enterprises, and the like in order to avoid interference in the bleaching by soot, dirt and obnoxious vapors and fumes. The hand labor required would be tremendous, and at the present time this means either an absurdly high cost or a very low scale of labor conditions. The results to be obtained in linen bleaching are to produce a white of satisfactory clearness and tone, while maintaining the strength of the fiber and its other qualities of luster and feel. Furthermore these qualities must be permanent, that is to say, the bleached white must not in time turn yellow, or the strength must not deteriorate on storing due to the effects or residues of chemicals. There is no doubt but that a purely chemical treatment capable of rational control can be devised to furnish these results and at the same time take the place of the irrational and cumbersome and time-consuming methods of grass bleaching.

The following methods for the bleaching of various qualities of linen have been selected from Tailfer:

(a) Light Handspun Cambrics.

(1) Steep in hot water 12 to 24 hours; hand-wash, and squeeze.

(2) First lye boil, 8 to 10 hours with salt of soda 2° to 3° Tw., with rosin soap, without pressure; wash in kier and squeeze.

(3) Sour with hydrochloric acid 5 liters per 1000 of water; temperature 80° F.; hand-wash, and squeeze.

(4) Second lye boil, same as first; wash in kier, and squeeze.

(5) Grass for 24 hours.

(6) Wash in stocks with olein soap, and third lye boil same as second; wash in kier, squeeze.

(7) Grass for 24 hours.

(8) Wash with soap and give 4th lye boil like third.

(9) Grass for 24 hours.

(10) Sort pieces. first lot to be chemicked; second lot to be washed with soap in stocks, given fifth lye boil with salt of soda, and grassed.

(11) First chemic of 0.15° chlorometric strength; temperature 75° F.; steep 5 hours; hand-wash, and squeeze.

(12) Sour with sulfuric acid 3 parts per 1000 of water; temperature 80° F.; hand-wash, and squeeze.

(13) Boil with olein soap, follow with lye boil (salt of soda 2° Tw.); wash in kier, and squeeze.

(14) Grass for 24 hours.

(15) Second chemic of 0.1° to 0.2° chlorometric strength, temperature 75° F.; steep 5 hours; hand-wash; squeeze.

(16) Sour with sulfuric acid same as before.

(17) Lye boil with salt of soda 2° Tw., with olein soap.

(18) Hand scour with white or olein soap.

(19) Sort: first lot, wash in hot water, and grass; second lot, lye boil with salt of soda 2° Tw.; wash in kier, and grass.

(20) Sour with hydrochloric acid 4 parts per 1000 of water; temperature 80° F.; hand-wash; squeeze.

(21) Boil with olein soap, and hand rub.

(22) Sort.

(23) Third chemic of 0.08° to 0.1° chlorometric strength; temperature 75° F.; steep 3 to 4 hours; hand-wash; squeeze.

(24) Sour with sulfuric acid as after first chemic; wash carefully.

In the chemicking it is recommended to use sodium hypochlorite in place of chloride of lime, and it is important that the goods be squeezed before steeping, otherwise the action of the chemic will be inappreciable.

(b) Light Machine Spun Cambrics.

(1) Steep in hot water; hand-wash; squeeze.
(2) Boil with 6 lbs. lime per 100 lbs. goods for 6 hours; wash; squeeze.
(3) Sour with hydrochloric acid 5 parts per 1000 of water; wash; squeeze.
(4) Boil with salt of soda 3° Tw., with rosin soap; wash in kier; squeeze.
(5) Grass for 24 hours.
(6) Wash with soap on rubbing boards, and third lye boil with salt of soda 3° Tw.; wash in kier; squeeze.
(7) Grass for 24 hours.
(8) Boil with salt of soda 3° Tw., with rosin soap; wash in kier; squeeze.
(9) Grass for 24 hours.
(10) Sort: first lot, chemic; second lot, boil with salt of soda 3° Tw.
(11) Chemic at 0.15° chlorometric strength; steep 6 hours; wash; squeeze.
(12) Sour with sulfuric acid 3 parts per 1000 of water; wash; squeeze.
(13) Boil with olein soap, and lye boil with salt of soda of 2° Tw.; wash in kier; squeeze.
(14) Grass for 24 hours.
(15) Second chemic of 0.1° chlorometric strength; steep 6 hours; wash.
(16) Sour as before.
(17) Boil with olein soap; lye boil with salt of soda at 2° Tw.; wash in kier.
(18) Grass for 24 hours.
(19) Sour with hydrochloric acid 5 parts per 1000 of water; wash; squeeze.
(20) Boil with olein soap, and lye boil with salt of soda at 2° Tw.; wash in kier; squeeze.
(21) Sort: first lot, grass; second lot, boil with soda of 2° Tw., and grass.
(22) Sour with hydrochloric acid 5 parts per 1000 of water; wash; dry.
(23) Sort.
(24) Third chemic 0.08° to 0.1° chlorometric strength; steep 4 hours; wash; squeeze.
(25) Sour with sulfuric acid as before; wash, and finish.

(c) Boiled Yarn, Cambric Handkerchiefs and Household Linens.

(1) Boil 10 hours with 10 percent of lime on weight of goods; wash in stocks.
(2) Sour with hydrochloric acid 3° Tw.; wash in stocks.
(3) Boil 10 hours with salt of soda 5° Tw.; wash in kier; lye boil a second time, and wash in stocks.
(4) Grass for 2 to 3 days.
(5) Boil 10 hours in salt of soda 4° Tw., with rosin soap; wash in stocks.
(6) Grass for 2 to 3 days.
(7) Boil with salt of soda as in 5.
(8) Grass for 2 to 3 days.
(9) Chemic at 0.65° chlorometric strength; steep 3 hours; wash in stocks.
(10) Sour with sulfuric acid of 2° Tw.; wash in stocks.
(11) Scour with soap on rubbing boards; boil 6 hours with salt of soda 2° Tw.; wash.
(12) Grass for 2 days.
(13) Chemic and sour as in 9 and 10.
(14) Same as 11.
(15) Third chemic and sour same as before.
(16) Double wash in wheel and finish.

6. Bleaching with Sodium Hypochlorite.

The use of solutions of sodium hypochlorite in place of those of chloride of lime for the bleaching of linen goods is fast growing in the favor of the bleacher. This is especially true since the introduction of liquefied chlorine has provided the bleacher with an efficient and convenient method of preparing this reagent. As in the case of cotton it has been found in the bleaching of linen that the efficiency of sodium hypochlorite solutions is higher than that of solutions of

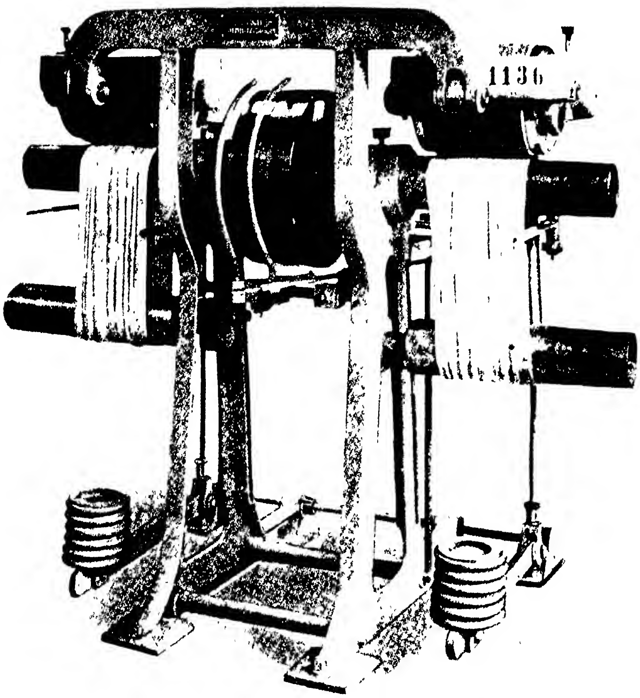


FIG. 279.—Yarn Treating Machine for Softening Linen Yarns.

chloride of lime of the same content of "available" chlorine. In the bleaching of linen with sodium hypochlorite it is advisable not to have the liquor too alkaline; consequently in preparing it from liquefied chlorine it is better to absorb the gas in a solution of caustic soda rather than in one of soda ash, as in the former case a more neutral solution can be prepared, while the latter requires a considerable excess of alkali. The use of sodium hypochlorite in linen bleaching makes it easier to remove all residues of the bleaching agent from the fiber than is the case when chloride of lime is used. It is also said

to give a softer and nicer bleach with a better preservation of the luster of the fiber.

Solutions of sodium hypochlorite for linen bleaching can also be prepared electrolytically and by the interaction of soda ash on a solution of bleaching powder. The preparation and use of such solutions has already been fully discussed under the subject of cotton bleaching and consequently will not be repeated here.

7. Grass Bleaching.

The exposure of cloth to the action of air and sunlight on the grass was the oldest method of bleaching and was largely practised in the case of linen, and in fact, even to-day linen in some countries is

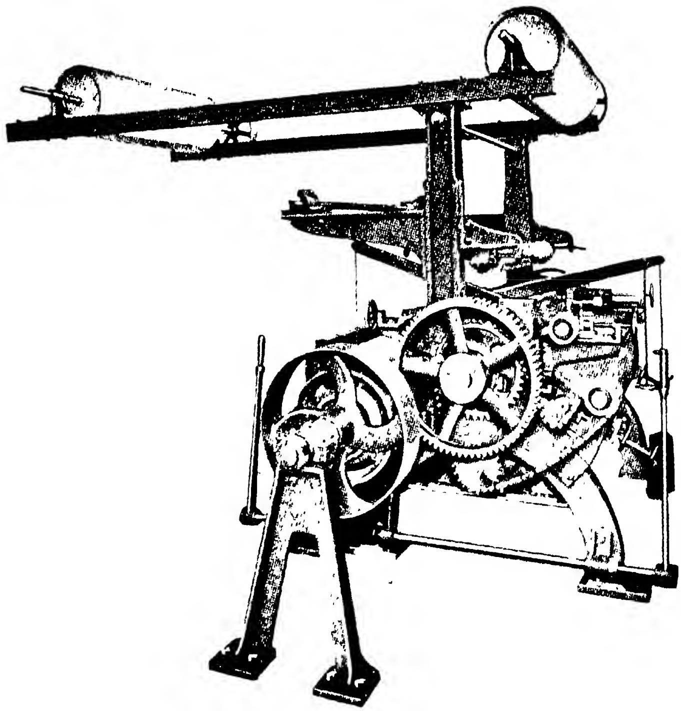


FIG. 280.—Tommy Dodd Mangle for Linen and Cotton Goods (Text. Fin. Mchy. Co.).

bleached by a modification of this process. To obtain a good bleaching by grassing, however, required an exposure lasting for a month and interrupted by frequent boiling of the goods in water or alkaline solutions. Such a process is no longer practicable in most places, as it requires too much time and attention and calls for the occupation of a

large acreage of meadow lands. Furthermore, it was not possible by simple grass bleaching to obtain a pure snowwhite, this requiring the aid of chemical bleaching agents. On this account pure white linen was looked upon with disfavor, and even at the present time, most linen goods are only given a half or three-quarters bleach with hypochlorites, so as to simulate the traditional grass bleach of former days.

The bleaching of linen by grassing is conditioned by four elements, namely: light, air, moisture, and the nature of the grass. Light, especially direct sunlight, appears to be the most effective bleaching agent, as fabrics are noticed to bleach much more rapidly in bright sunny weather than during dull cloudy days, and also better by day than by night. If fabrics contain colored yarns, it is better not to expose them to direct sunlight on the grass, but only to grass the goods during the morning and evening, as most colors will fade otherwise. Dry weather is not very favorable to grassing; a slightly moist atmosphere so that dew is deposited in the morning is the most suitable. Ireland is especially suited for the grassing of linen, and on this account its bleached fabrics are renowned the world over. When linen is hung on lines so that it is removed from the grass it does not bleach as well as when placed directly on the grass itself; it is not known exactly how the grass assists in the bleaching, but it is probably due to the moisture and oxygen or ozone exhaled by the plants.[8] In some cases the goods after being stretched out on the grass are systematically sprinkled with water, but this is rather a costly proceeding, and can only be used for special goods.

Though cotton can be thoroughly bleached without exposure to the grass, no method has yet been devised for entirely dispensing with it in the case of linen goods of the highest quality.

In the grassing process of bleaching linen it is very important that the cloth be well spread on the green and that the selvedges be kept out without curling up. For this purpose pins are put in at each end of the piece and also four rows of cross pins. If the weather becomes very hot the cloth should be lifted before the dew rises from it, and in windy weather the pins must be taken out or the cloth may be torn. In winter time the grassed cloth is often frozen stiff, and it must not be lifted when in this condition, as if doubled or folded it

[8] Begeman considers that unbleached cloth has a yellowish color because it reflects the chemically inactive yellow rays of light; therefore, he suggests that by bluing the cloth this influence could be neutralized and that in grass bleaching the tinted cloth would become more subject to the chemically active blue rays of light The blue tint was obtained by using a solution prepared by rinsing 4 pounds of milk of lime with 1 pound of finely pulverized Indigo, and then adding 4 pounds of ferrous sulfate The cloth is first boiled for 4 hours in a solution of silicate of soda of 1° Bé After this it is well washed and tinted slightly with the bluing solution. It is claimed that by this process the period of grassing is reduced to about one-half that ordinarily employed

It is stated that this process renders the action of the sunlight more effective by absorbing the red rays and increasing thus the proportion of violet rays The actual amount of the latter, however, is in no wise increased by such a condition, and it is doubtful if the Indigo has any other effect than that of simply giving a slight bluish tint to the fiber, and thus increasing the apparent brilliancy of the white color by neutralizing the yellowish tint. According to later observations, Indigo is really a poor sensitizer for grass bleaching, and it is now claimed that chlorophyll (the natural green coloring matter present in plant leaves) is much more effective in accelerating the bleaching action Other ingenious methods have also been proposed in the rather long array of patent literature on this subject. Saturating the fiber with turpentine and other oil preparations previous to exposure to the bleaching green has been proposed. None of these assisting processes, however, seem to have had any practical value.

will crack and cut. The greatest care must be taken at every stage to prevent the cloth from getting dirty or damaged.

Without doubt the active agent in grass bleaching is ozone and hydrogen peroxide. Just what agencies cause the formation of atmospheric ozone is not altogether understood. It is supposed that in the evaporation of moisture in the presence of light there is a small amount of ozone formed, though it is more probable, perhaps, that hydrogen peroxide is formed. Dry air has little or no bleaching action, but the evaporation of the moisture from grass and the soil as well as from the moistened cloth itself provides the conditions for the formation of hydrogen peroxide in the presence of sunlight, it being

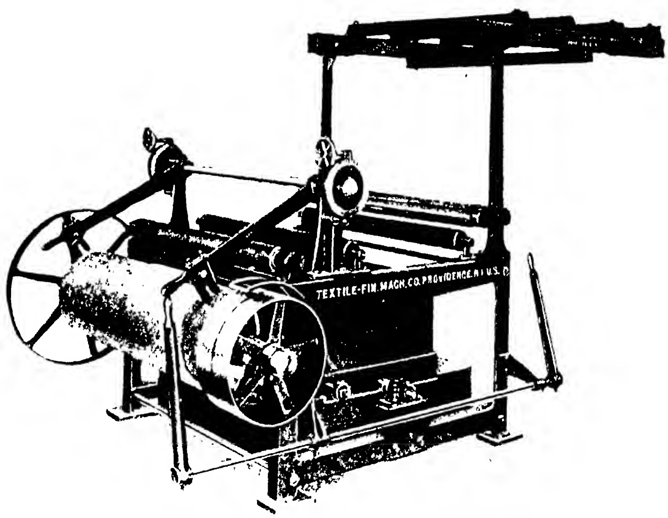


FIG. 281.—Sprinkler for Linen and Cotton Goods (Text. Fin. Mchy. Co.).

supposed that the blue and violet rays of the latter exert a catalyzing effect in the reaction.

Grass bleaching, of course, is dependent to a great extent on the condition of the weather. The bleaching effect is most active in the morning sun when dew is present on the grass and the cloth. The bleaching power of the sunlight also varies considerably with the period of the year, being most active, of course, in the summer time. In fact, in winter it may require an exposure of many weeks to obtain a degree of bleaching that in summer can be obtained in as many days. The temperature also has a considerable influence on the rapidity of grass bleaching, the low temperature in winter lessening considerably the activity of the hydrogen peroxide present.

The cause of the special bleaching activity of meadows in certain

localities has been attributed by Gardena [9] to a higher radio-activity of the soil. It is supposed that the presence of traces of radium or other radio-active substances favors the formation of hydrogen peroxide and ozone. To test this, however, bleaching experiments have been conducted in the presence of strongly radio-active salts and no appreciable effect has been observed. The more probable reason that some bleaching greens give better results than others is to be found in the better quality of the water and air and the more intelligent methods of handling the goods. Differences in the humidity of the air, quantity of dew formation, proportion of sunshine, amount of atmospheric precipitation in rain, fog and snow, also have much influence on the efficiency of a bleaching green. Also of considerable influence is the alkalinity of the fiber. As alkalinity has been found to accelerate the bleaching, Tailfer has recommended that the cloth be treated with a solution of caustic soda and soap previous to exposure on the bleaching green.

Though it is generally supposed that grass bleaching has little or no deleterious action on the fiber itself, this is not altogether true. Leimdörfer [10] carried out experiments on linen with 28 days exposure and found:

loss in weight	= 6.1	percent
loss in elasticity	= 5.2	"
loss in strength	= 36.2	"

It is also recognized among bleachers that prolonged exposure on the grass in a hot summer sun is very liable to cause serious damage to the goods.

8. Ozone Bleaching.

Since it has been supposed that ozone plays a considerable part in the action of grass bleaching, attempts have been made to shorten the time required and to control the process by using air charged with definite small amounts of ozone prepared by electric discharges.[11] Several forms of very efficient ozonizing apparatus have been constructed by the leading manufacturers of electrical machinery both here and abroad, and very exhaustive experiments have been made with the use of ozonized air in bleaching. It is found that the best results are obtained by impregnating the goods with dilute ammonia water and then exposing to the action of the ozonized air in suitable chambers. Only a very small proportion of ozone may be used, as other-

[9] *Leipz. Färber-Zeit*, 1906, p. 427.

[10] *Chem. Zeit.*, 1912, p. 526.

[11] It is said that the combined ozone-hypochlorite bleaching process for linen has been developed successfully in a Silesian bleach works. In regard to the bleaching of linen by means of ozone, the Greiffenberg Bleachery in Silesia report the following commercial process: The goods are run through a bath of dilute hydrochloric acid and then exposed in the moist state in chambers to the action of ozonized air for about seven hours. For a three-quarter bleach only one such treatment is required, but for a full bleach from two to three treatments are necessary, and these are usually alternated with the operations of the ordinary bleaching process for piece goods. In order to obtain good results with ozone bleaching it is necessary to admit sunlight into the bleaching chamber, or if this is not practical the electric arc light may be used. It is said that one day's treatment in the ozone chamber is equivalent to three days' exposure on the grass. As far as cost is concerned it is said that the ozone bleaching is no cheaper than grass bleaching, but it is more convenient.

wise the fiber will be seriously damaged. It has been found that 1 day of ozone bleaching is about equivalent to 3 days of grass bleaching in summer or 14 days in winter, and also as the ozone treatment is independent of sunlight it may be carried out during the night.[12] Notwithstanding the considerable effort made to introduce the ozone method of bleaching it does not seem to have met with any degree of commercial success in competition with the other established methods of bleaching.

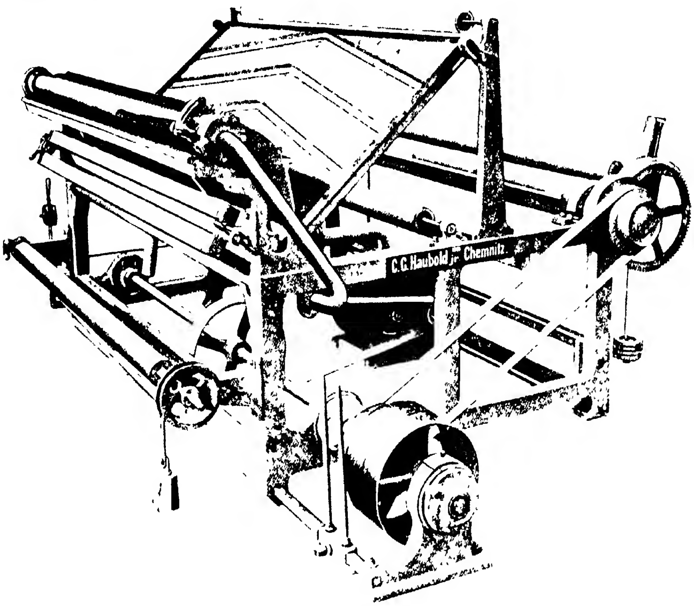


Fig. 282.—Damping Machine for Linen and Jute Fabrics.

9. Special Methods of Bleaching Linen.

In the Cross and Parkes process for bleaching linen[13] an attempt is made to get away somewhat from the old traditional methods of kier boiling with lime. The linen pieces are run at full width at a temperature of 120° F. through a solution containing 1¾ lbs. soap, 14 lbs. sodium silicate, 1½ lbs. caustic soda, 1¾ lbs. clear mineral oil and 10 gallons of water. After thorough impregnation with this solution they are run into a chamber containing steam at atmospheric pressure and wound up on a roller. The goods are then steamed with dry steam at a pressure of about 4 lbs. for 1 to 4 hours, and then boiled (while still in the chamber) with soda ash or silicate of soda under pressure.

[12] *Ger. Pats.* 17,117 and 78,839; also Schneller, *Leipz. Monatsch. Textil. Ind.*, 1894, p. 204.
[13] *Jour. Soc. Dyers & Col.*, 1901, p. 38.

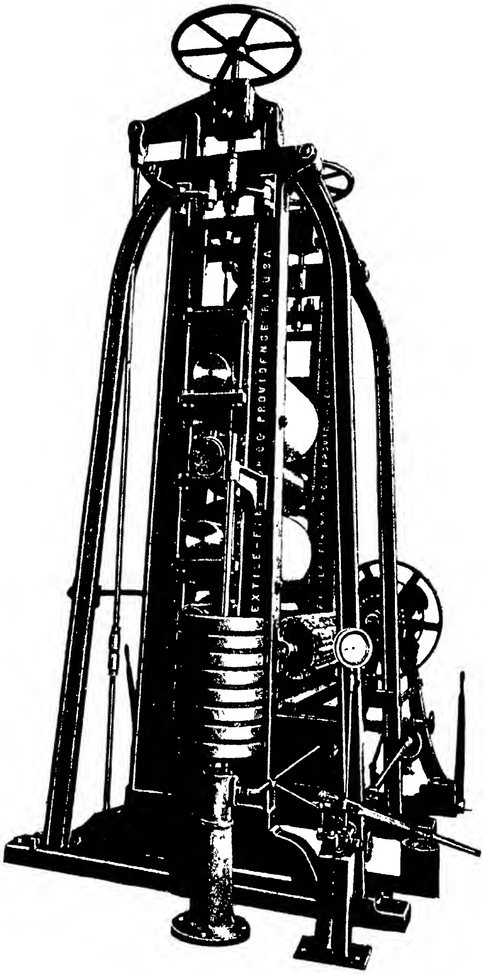


Fig. 283.—Five Roll Hydraulic Pressure Calender for Linen, Cotton, and Jute Goods (Text. Fin. Mchy. Co.).

After the boil is finished the goods are well washed, and then are in a condition suitable for bleaching by chemicking or grassing.[14] In a

[14] There have been a large number of new processes suggested or patented for the bleaching of linen. Schreiner (*Ger. Pat.* 52,205) uses ozonized oil of turpentine; Brins Oxygen Co. (*Ger. Pat.* 46,811) uses chlorine gas or chlorine solutions mixed with oxygen; Tessié du Motay suggested solutions of potassium permanganate; Jacobson (*Ger. Pat.* 21,081) uses barium peroxide with the addition of sodium silicate or borate; Tabary (*Ger. Pat.* 101,285) uses nitrous acid; Bregeard (*Ger. Pat.* 20,177) suggests the addition of zinc sulfate to the

process described by Keukelaere [15] the linen cloth is first scalded for ½ hour in a solution containing 5 to 15 percent of sodium sulfide, and then rinsed in water containing ½ percent of sulfuric acid (on the weight of the goods). This operation of scalding is repeated several times and the bleaching is then proceeded with. Jardin [16] recommends the use of nitric acid for the bleaching of linen to take the place of the grassing. The goods are steeped for about 5 hours in a solution containing 5 gallons of nitric acid to 1000 gallons of water.

In the production of linen pieces in the form or color of what is known as "Brown Hollands," the goods are usually not dyed in order to obtain this shade, but the unbleached linen is run through a warm solution of stannous chloride acidulated with sulfuric acid. An acid solution of titanous chloride may also be employed for the same purpose.

9. Testing of Bleached Linen.

Bleaching linen by chemical means always deteriorates the fiber more or less, and the very best and highest class of linen goods are only bleached to a partial degree by grassing for long periods of time. The action of chloride of lime causes the linen fiber to become chlorinated to a certain extent, and this fact is of service in the testing of linen goods to ascertain if they have been bleached with this agent or not. The test may be carried out in the following manner: Boil a sample of the suspected linen with moderately concentrated nitric acid, filter, and to the clear filtrate add a few drops of a solution of silver nitrate. The formation of a white precipitate will indicate the presence of chlorine, which will show that the material was bleached with the use of chloride of lime; if no white precipitate is formed there is reasonable certainty that chloride of lime has not been used. Of course, this would not eliminate other chemical methods of bleaching, such, for instance, as with potassium permanganate, but this method is seldom met with commercially. Also in linen bleached with chloride of lime, there will generally be a much higher percentage of lime present in the ash than with pure linen.

In the bleaching of linen it frequently happens that yellow spots remain in the material, although the soap, soda, etc., which have been used in the process were perfectly pure. It is the opinion of Geisenheimer [17] that these spots are due to the use of hard water, which on boiling precipitates calcium carbonate on the goods, and this fixes the coloring matters contained in the lyes. He recommends the addition of sodium silicate to the hard water. This is effected by adding to the soda ash from 10 to 20 percent of soluble glass. Such a mixture

hypochlorite bath; Cross and Parkes suggest steaming with a mixture of caustic soda, sodium silicate, and an oil-soap emulsion; Lagage introduces carbon dioxide gas into the chloride of lime bath; Martin has patented a whole series of bleaching processes describing the use in the kier liquor of turpentine oil, carbon tetrachloride, benzine, and sodium nitrate. Schott (*Ger. Pat.* 88,945 and 124,677) uses sulfurous acid in a specially constructed bleaching apparatus. Keukulaere (*Ger. Pat.* 169,448) employs repeated boilings with 5 to 15 percent of sodium sulfide.

[15] *Jour. Soc. Dyers & Col.*, 1905, p 275.

[16] *Jour. Soc. Dyers & Col.*, 1904, p. 105.

[17] *Comptes rend.*, 1894, No. 118.

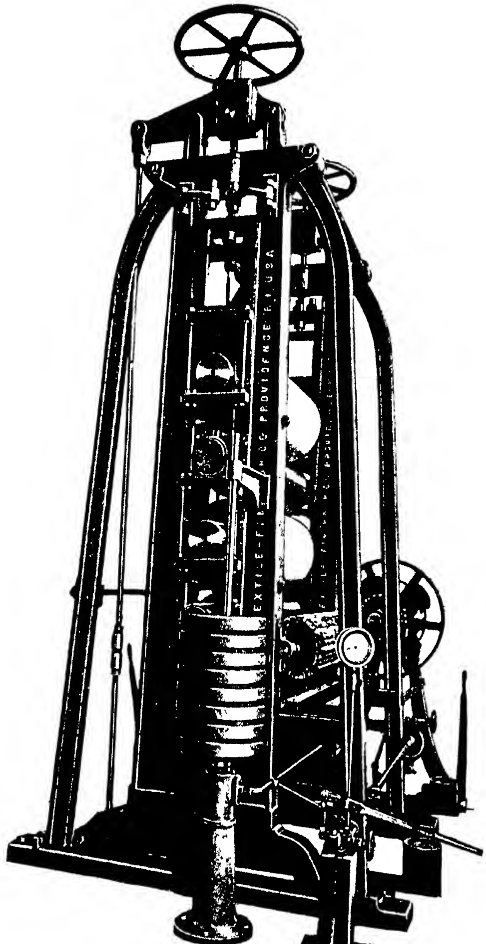


FIG. 283.—Five Roll Hydraulic Pressure Calender for Linen, Cotton, and Jute Goods (Text. Fin. Mchy. Co.).

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These oils resist the bleaching operations and are very difficult to remove.

In the bleaching of linen it has been noticed that after the fiber is chemicked it is almost impossible even by prolonged and intensive rinsing to remove all traces of "active chlorine" so that the fiber will no longer give the potassium iodide-starch reaction. One explanation of this fact was that the linen fiber perhaps retained the chlorine in the same manner that wool persistently retains sulfur dioxide. Another explanation was to the effect that cellulose peroxide was formed, and this body reacted with the potassium iodide-starch solution in the same manner as "active chlorine." It has been rather surprising to find that bleached linen goods, even after several months, still give the chlorine reaction, although it is almost impossible to suppose that such an energetic and reactive agent as chlorine could be retained thus for such a length of time, and the subsequent rotting of the fiber and the development of free acid would be expected. Raschig,[18] however, has shown that chlorine in dilute solutions combines with amino bodies to give products called *chloramines* (NH_2-Cl type). Since the linen fiber contains quite an appreciable amount of albuminous bodies of an amino nature, it is probable that in the bleaching some of these chloramines are formed, and they react with potassium iodide-starch solution in the same manner as "active chlorine." This condition is particularly liable to occur in linen that has been only partially bleached. Cross and Bevan have shown that in normal commercial samples of creamed linen yarn there was found as much as 0.1 percent of "active chlorine," combined no doubt as a chloramine. The amount of chlorine thus held will depend on the degree of purification of the fiber, and should be absent from completely bleached linen, as this should not contain any residues of albuminous matter.

Chloramine is readily decomposed by the action of sulfurous acid (sodium bisulfite, antichlor) according to the following equation:

$$2NH_2Cl + 2H_2SO_3 + 2H_2O = (NH_4)_2SO_4 + H_2SO_4 + 2HCl$$

Therefore, bleached goods that have been treated with sodium bisulfite solution as an antichlor are little likely to show any evidence of the presence of chloramine. Ammonia also acts as an antichlor in this same sense, as it leads to the decomposition of the chloramine. Hydrogen peroxide, on the other hand, though it neutralizes any hypochlorite, will not decompose the chloramine; in fact, owing to this reaction, hydrogen peroxide treatment can be used to distinguish between "active" chlorine present as hypochlorite and that present as chloramine.

An interesting feature concerning chloramines is that in old standing bleach baths for linen these bodies accumulate. The formation of the chloramine is in proportion to the amount of nitrogenous or albuminous matter present in the fiber. With the rather impure fiber first entering the bleach liquor some of the chloramine formed will dissolve into the bath, but as the latter accumulates chloramines there

[18] *Chem. Zeit.*, 1907, p. 920.

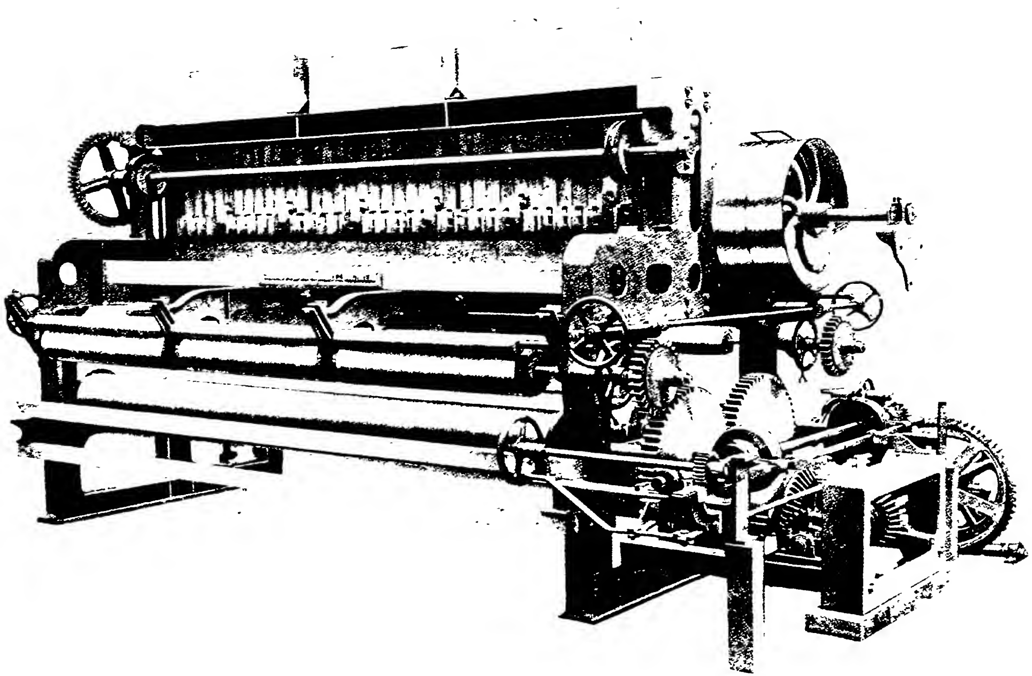

Fig. 285—Two Roll Beetling Machine with Wooden Fallers (German Type).

is a tendency for the pure bleached cellulose fiber to take up these bodies again after the manner of a mordant. In this way it will be seen that it is difficult to obtain a full bleached linen fiber entirely free from chloramines.

The question would naturally arise as to whether the "active" chlorine in the chloramine bodies is sufficiently reactive to convert cellulose into oxycellulose, and thus cause a tendering or rotting of the goods. This question is left undecided in the discussion of Cross and Bevan, though they point out the danger resulting from the presence of free acid which nearly always accompanies the chloramine, since the decomposition of the chloramine results in the formation of free hydrochloric acid. This would, therefore, indicate that the presence of chloramines in bleached goods would ultimately endanger the strength of the material.

The chloramine reaction is a good test for the quality of the bleach and is valuable in the comparison of different bleached samples.

10. Bleaching with Permanganates.

The use of potassium permanganate has also been suggested for the bleaching of linen. It is said that the permanganate acts more quickly than chloride of lime on the coloring matter and some claim it has less action on the fiber.

Schmidt[19] gives the following method for using the permanganate bleach on linen: The linen yarn is first boiled-out with 5 percent of soda ash; washed; boiled-out again in the same manner; then steeped in a bath containing 1 percent of potassium permanganate; rinsed; stripped with a dilute solution of sodium bisulfite (2° Bé.); rinsed; boiled-out a third time with 2½ percent of soda ash; rinsed; bleached again with permanganate as before; rinsed; stripped with sodium bisulfite; rinsed; boiled-out a fourth time with 2½ percent of soda ash; rinsed, treated again with permanganate and sodium bisulfite, repeating the operation in this manner until a desired degree of whiteness is obtained. The permanganate solution should not be more concentrated than about 1 pound to 1000 gallons of water and should be slightly acidified. When bleached in this manner the linen yarn is said to lose about 20 percent in weight, and for the entire bleaching 100 pounds of yarn will require about 9 pounds potassium permanganate, 7½ pounds sulfuric acid and 11½ pounds sodium bisulfite (38° Bé.).

The treatment with the permanganate solutions is carried out in the cold, and sulfuric acid in the baths gives better results than hydrochloric acid, besides being considerably cheaper.

Sometimes the permanganate bleach on linen is used in connection with grass bleaching in order to hasten the process, or in case bad weather does not permit of suitable exposure to the bleaching green. Another method recommended for the bleaching of linen with potassium permanganate is the following: After being steeped as ordinarily the linen is steeped for 15 to 20 minutes in a solution of permanganate (4 to 6 percent on the weight of the goods), and mag-

[19] *Monit. Scientif.*, 1902, p. 219.

nesium sulfate. This causes the material to become brown from the precipitated oxide of manganese. This is removed, and the goods whitened by passing through a solution of sodium bisulfite. These

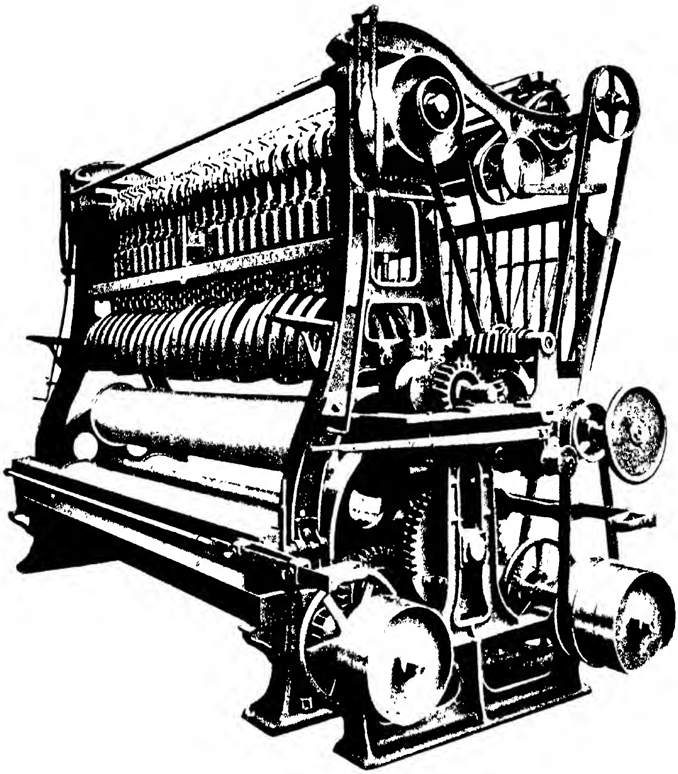

FIG. 286.—High Speed Spring Beetling Machine (English Type).

operations are repeated until a satisfactory white is obtained. The process is said to be operated successfully in France, and by its means the linen is bleached in about 3 days, while under the old methods the time required is 3 to 4 weeks.[20]

[20] According to Martin, an advantageous method for the bleaching of linen or jute consists in boiling such fabrics with 8 percent of caustic soda containing 1 percent of turpentine, washing, and then working for two hours in a bath of chloride of lime at 2° Bé., and containing as an addition 2 percent of aluminium sulfate in solution. The fabrics are then washed, and boiled for two hours in a solution containing 3 percent of caustic soda and 1 percent of benzine; washed again, and treated for four to six hours in a bath of chloride of lime at ½° Bé., and containing 0.2 percent of aluminium sulfate. The cloth is then slightly acidulated, and boiled for two hours in 2 percent of caustic soda and 0.2 percent of benzine. A third treatment with chloride of lime at ¼° Bé. is then given, with the addition of 0.1 percent of aluminium sulfate. The material is finally soured and washed. Just what effect the addition of the small amount of aluminium sulfate to the bath of bleaching powder would have is not quite apparent; it would form a small quantity of aluminium hypochlorite with the consequent precipitation of a corresponding amount of calcium sulfate. Also, the purpose of the addition of benzine to the caustic soda bath is rather imaginary, to say the least.

11. Bleaching with Peroxides.

Solutions of hydrogen peroxide (prepared either from hydrogen peroxide itself or from sodium peroxide) may be employed for the bleaching of linen in practically the same general method of procedure as for cotton or other vegetable fibers. Owing to the fact, however, that linen is much more highly colored and is far more resistant to the action of bleaching agents than cotton the methods for bleaching linen with peroxides must be extended to longer periods of treatment, as well as repeating the process a sufficient number of times in order to produce the desired degree of whiteness. This makes the use of peroxides for linen bleaching a rather expensive and tedious operation. The action of the peroxide in the bleaching of linen, however, is very similar to that of the grassing of the material in the older forms of bleaching. The effect is mild and results in but little injury

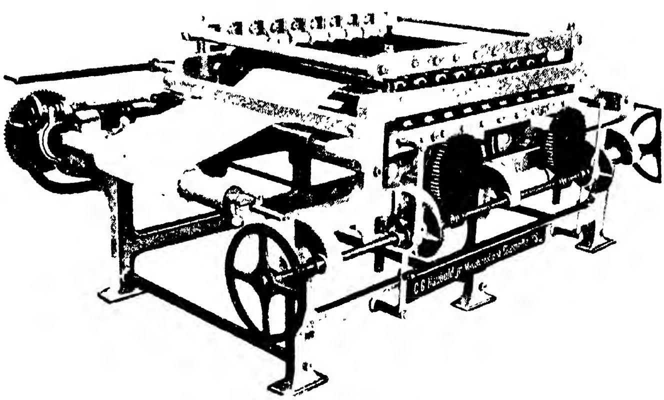

FIG. 287.—Button Breaking Machine for Smoothing Unions, Half-silks, etc.

to the fiber. In order to obtain a full white, and also as a means of hastening the process, a hypochlorite bleaching may be employed as a preliminary operation previous to the treatment with the peroxide bath; or several such treatments may be alternated with rinsings in dilute acid baths (sours).

Just previous to the outbreak of the war there appeared in the European market a concentrated form of hydrogen peroxide solution containing 15 percent of the peroxide which was especially recommended for the half-bleaching of linen, and the following method of operation was recommended by the manufacturers: To 100 gallons of pure soft water add ½ gallon of hydrogen peroxide (15 percent), ½ gallon of ammonia water and 2 pounds of Monopol Soap. Steep the goods in this alkaline bath, starting cold, and after 6 hours heat to 110° F., and leave at this temperature overnight. Run out the goods and freshen the bath with ½ gallon of hydrogen peroxide (15 percent) and ¼ gallon of ammonia water. Be certain that the bath still shows

an alkaline reaction. Re-enter the goods and continue the bleaching at 110° F. After about 20 hours the linen should be satisfactorily bleached; the goods are then removed and well rinsed, first in water slightly acidulated with acetic acid, and finally in pure water.

12. Effect of Bleaching on Linen.

Linen is quite different from cotton in regard to its alteration in weight and strength during the bleaching operation. In the case of linen there is so much foreign matter present that during the boiling-out process there may be a decrease of 30 percent in weight, whereas cotton usually loses only about 5 percent. There is also naturally a decrease in strength of the linen, but if the process of bleaching is properly conducted this decrease in strength and weight is almost entirely due to the boiling-out, and is therefore unavoidable. Higgins, in a series of tests on the loss in strength and weight of linen fabrics during the bleaching process obtained the following results:

Loss of Weight of Linen During Bleaching

	Weight in Grams	Loss Percent
Brown linen	92.1	—
After steeping	88.7	3.8
After lime-boiling	77.15	16.2
After soda-boiling	70.93	22.9
After chemicking	69.53	24.5
Fully bleached	67.52	26.7

This shows that the decrease in weight takes place principally in the boiling operations, the bleaching process proper, or chemicking, not causing a loss in weight to any great extent. These figures also show that the so called "half-bleaches" owe their weight entirely to the retention of much of the original impurities in the cloth. The following ash determinations show this fact:

	Ash Percent
Brown linen	1.28
After lime-boil	0.18
After soda-boil	0.084
After chemicking	0.08
Fully bleached	0.074
Half-bleached	0.37

The following table shows the loss in strength of linen during bleaching corresponding to the same tests given above for loss in weight:

	Tensile Strength Grams
Brown linen	1270
After lime-boil	960
After soda-boil	1070
After chemicking	930
Fully bleached	910
Decrease in strength	= 28.3 percent

It is to be noticed that the soda-boiling causes an increase in strength; this is no doubt due to the action of the alkali increasing the cohesion and consolidation of the fibers in the yarn.

Chapter XXV.

Bleaching of Other Vegetable Fibers and Materials.

1. General Considerations.

The other vegetable fibers besides cotton and linen which are used for textile purposes are seldom bleached, as they are employed for the manufacture mostly of rough and crude fabrics and are not frequently dyed in delicate colors. They nearly all contain a considerable amount of natural coloring matter, more or less associated with the constitution of the fiber itself, so that in bleaching the fiber to a perfect white it is chemically decomposed to a considerable extent, in consequence of which its strength and physical properties are seriously altered.

Jute, however, is coming to be used to quite an extent for the manufacture of woven articles, and as it possesses a dark brown color in its natural state, it is frequently desirable to bleach it to a greater or lesser degree. Hemp is also bleached at times in a partial manner for certain purposes. Some fibers, such as ramie, for instance, are so white in their natural condition that they require about the same character of bleaching as cotton. Straw, and similar fibers, are frequently bleached, sometimes to a complete white, though mostly only partially decolorized; but such fibers are almost altogether employed for hat-making, and can scarcely be included as textile materials.[1]

2. Bleaching of Jute.

Jute may be bleached after the general manner of cotton and linen. As jute, however, does not consist of pure cellulose like cotton, but of what is known as "lignocellulose," it suffers considerable alteration by bleaching with chloride of lime.[2] The fiber constituents appear to become chlorinated and physically altered.

[1] The following process has been put forward for the bleaching of jute or other vegetable matters: The material is immersed for a period not exceeding 2 hours in a solution of potassium permanganate not exceeding 1¼ percent in strength; then a solution of hydrogen peroxide of not more than 2 percent strength is added to the bath in such proportion as to cause the complete decomposition of the potassium permanganate remaining in the bath. After remaining for a further period of ½ hour, the material is removed and thoroughly washed If any manganese oxide is left on the fiber, it is removed by a bath of a weak solution of sodium bisulfite, after which the material is again washed. (*Eng. Pat.*, No. 10,424; 1895).

[2] The vegetable fibers, although consisting in general of cellulose, have the latter not only mixed with but actually combined with other substances, generally considered as alteration products of the cellulose Cross and Bevan classify these compounds in three groups: (1) lignocellulose, (2) pectocellulose, (3) adipocellulose. And these groups may be said to comprise the major portion of the extraneous material which it is the object of bleaching to remove or decolorize. The lignocelluloses are best represented by jute, which fiber consists almost entirely of those bodies. Lignocellulose gives the following characteristic reactions: (1) It combines energetically with chlorine, forming a chloride, the presence of which may be detected by the intense magenta-red color produced on the addition of sodium bisulfite. (2) Potassium iodide with sulfuric acid colors the lignocelluloses a deep brown. (3) Aniline hydrochloride gives a golden yellow color with lignocellulose. (4) The coal tar dyes in general have a strong affinity for lignocellulose (5) A solution of phenol in hydrochloric acid gives an intense red color with lignocellulose. (6) Potassium ferricyanide gives a deep blue color.

The following method is carried out in England for obtaining a "half bleach" on jute yarn: The hanks are worked in a solution of bleaching powder at 8° Tw. for one hour at a temperature of 80° to 100° F., attempting as far as possible to keep the material submerged beneath the surface of the liquor and not exposed to the action of the air. The jute is then removed from the bleach liquor, allowed to drain and is then washed. The next operation is to work the material in a bath of sulfuric acid at 4° Tw. for 30 minutes, and finally wash well in several changes of water. To obtain a lighter color on the yarn, these operations are repeated several times, if necessary. Another method of bleaching jute yarn is to use a series of three bleach liquors, the first containing 15 to 20 percent of bleaching powder (on the weight

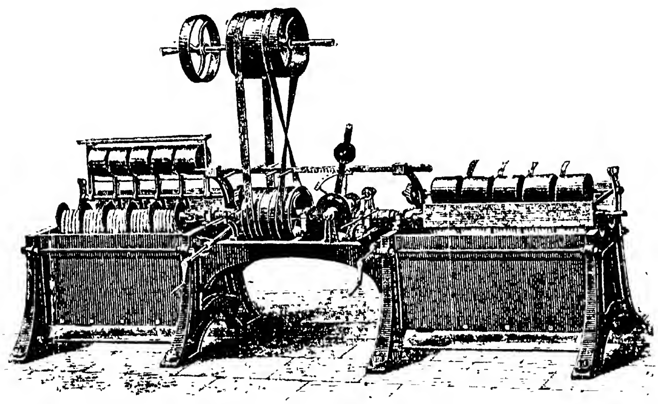

FIG. 288.—Skein Machine for Jute Scouring and Bleaching.

of the jute); the second 10 to 15 percent; and the third 10 to 5 percent. The yarn is steeped in each tank about 45 minutes at a temperature of 120° F., after which it is washed and passed through a bath of sulfuric acid at 1° Tw., in which it is steeped for one hour. It is finally well washed to remove the acid.

Jute has also been bleached by the use of sulfuring or stoving process whereby the fiber is exposed to the action of fumes of burning sulfur (sulfurous acid) in a manner similar to the bleaching of wool. This has the effect of lightening the color and also increases the luster of the fiber and gives it a better feel. The hanks of yarn are hung up on poles in a sulfur chamber, and it requires about 1 lb. of stick sulfur for each 100 lbs. of jute. New jute is sulfured more readily than old jute, therefore unless well blended together in the yarns, the fiber from different seasons will come up streaky. If jute after sulfuring is dampened it becomes quite yellow in color, and as this particular tone is sometimes especially desired, the bleacher sometimes steams the yarn after sulfuring in order to give it the required degree of moisture to produce the yellow color.

In bleaching jute, the yarn usually appears very uneven after treatment with the first solution of chloride of lime, on which account the three-bath process is to be recommended. If left too long in the first bath the yarn is liable to become tendered. The manner in which the yarn was spun also has considerable influence on its behavior in bleaching; if mineral oils have been used in the spinning, it is necessary to first steep the yarn in hot water, or to scour it out in alkaline solutions. Under other conditions, jute is rarely treated with alkalies previous to bleaching, the chief reason being that it occupies too much time and is too expensive, and also the yarn loses too much in weight, while the final results of bleaching are but slightly enhanced by the alkali treatment. The loss in weight sustained by jute when bleached with chloride of lime and without being boiled out with alkalies is from 6 to 8 percent.

According to Beltzer[3] from the point of view of bleaching the principal factor in the treatment of jute is the lignin complex. These bodies combine with chlorine forming products soluble in water. The formation and removal of these chlorinated products destroys the cohesion of the ultimate fibers with the result that the fabric is weakened. The guiding principle in the application of hypochlorites is therefore to avoid chlorination and to confine the action entirely to one of oxidation. To insure this it is very important to avoid acidification of the hypochlorite liquor and to maintain a neutral or even slightly basic reaction. The bleaching of jute by the use of nascent oxygen alone may also be effected by the use of peroxides or perborates in neutral, alkaline or acid solution. A satisfactory bleach liquor may be prepared with a solution containing 5 grams of sodium peroxide and 1 gram of sodium sulforicinoleate (Tetrapol) per liter. The latter ingredient makes for better penetration and equalization of the bleach liquor. The cloth is run back and forth between squeeze rolls in this bath at a temperature of 85° to 105° F. for about 2 hours. It is then rinsed and steeped in a stock solution containing 1 liter of sodium bisulfite liquor and 50 grams of oxalic acid per 10 liters for 8 to 10 hours at a temperature of 160° to 175° F. In order to obtain better bleaching the cloth may be subjected to two treatments with the peroxide bath with an intermediate sour and finally given a finishing steep in a solution of 5 to 10 grams per liter of sodium hydrosulfite at 70° to 80° F. for 12 hours, as this improves the color. A cheaper bleach may be obtained by substituting hypochlorite for the first peroxide bath, the cloth being run in a neutral or basic solution of hypochlorite containing a little Tetrapol at a temperature of 85° to 105° F. Then without washing it is run into a solution containing 3 grams per liter of sodium peroxide at the same temperature and is then finished with a treatment with acid bisulfite as before. The cheapest method, but one which gives inferior results is to give a hypochlorite bleach, then an ammoniacal "antichlor."

Cross and Bevan recommend the following process for the bleaching of jute pieces: The goods are first treated with a solution of silicate of soda containing 5 lbs. per 100 gals. of water at a temperature of 160° F. They are then passed through a solution of sodium hypo-

[3] *Bull. Soc. Chem.*, 1910, p. 294.

chlorite containing between 0.7 and 1 percent of available chlorine. The presence of soda is said to completely prevent the formation of chlorinated products. After being well washed, the pieces are next passed through a solution of hydrochloric acid at ½° Tw. to which a small amount of sodium sulfite has been added. The object of this is to remove any basic compounds which might subsequently cause a discoloration of the fiber through the action of oxidizing agents, and also to remove any salts of iron. After the acid bath, wash well. The goods should now be of a light cream color, have a soft handle, and be of good luster, and they are ready to be dyed. If the pieces are required for printing, they must be subjected to the following additional process: Pass through a bath of sodium bisulfite containing from 1 to 2 percent of sulfurous acid. Squeeze out the excess of liquid, allow to lie for 2 to 3 hours, and finally dry on steam cylinders. In

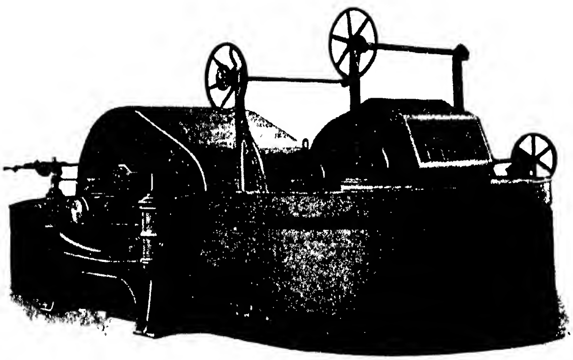

FIG. 289.—Hollander for Bleaching and Washing Paper Pulp.

drying, the sulfurous acid is driven off and the material is left impregnated with a neutral sulfite of soda which protects the fiber from the oxidizing influences to which it is exposed during steaming, but does not prevent the development of the colors.

Bleached jute appears to undergo certain changes on exposure to the air, as it gradually becomes darker in color and turns brown, while the fiber itself becomes harsher and more brittle, though if properly bleached it is only slightly tendered.

The statements to be found in many text-books that the ordinary methods of bleaching vegetable fibers with chloride of lime are not applicable to jute on account of this fiber rapidly absorbing chlorine and being thereby decomposed are misleading and erroneous, as the quality of the fiber does not appear to be very materially injured by bleaching in this manner, and the natural color may be almost completely removed.

The difficulty in the bleaching of jute with hypochlorites lies appar-

ently in the fact that the lignocellulose bodies in the fiber combine chemically with chlorine to form "chloramines" which are persistently retained by the fiber even after souring and very thorough washing. The chlorine retained in this form gradually reacts on the fiber on exposure to the air, resulting no doubt in the formation of hydrochloric acid or other destructive compounds, with the result that the fiber is gradually rotted. According to Hummel, solutions of sodium hypochlorite do not have this effect, and can be used therefor with better results than solutions of chloride of lime; but this is to be questioned, as "chloramine" bodies are no doubt formed with sodium hypochlorite as well as with any other hypochlorite. By the use of the permanganate bleach, the formation of "chloramines" is avoided, and nothing is left in the fiber which should prove subsequently to be injurious. The first action of the permanganate bleach, however, is much more severe than the hypochlorite, and consequently care must be exercised in this treatment to avoid tendering of the goods through over-oxidation of the fiber and the cementing tissues.

Potassium permanganate does not appear to be a good agent for the bleaching of jute, as it does not decolorize the fiber as well as chloride of lime, and it also seriously injures the strength of the jute by too strong an oxidation. It may, however, be used in connection with the hypochlorite bleach in the following manner:[4] The material is steeped over-night in water, then squeezed and well washed, after which it is boiled for 1 hour in a bath containing 5 pounds of soda ash to 100 gallons of water, squeezed and washed again. It is next steeped for 10 hours in a solution of bleaching powder of ¾° Tw. strength; squeezed and steeped in hydrochloric acid of ¾° Tw. for 1 hour, squeezed and washed well. It is next steeped for 1 hour in a bath containing 2½ pounds of potassium permanganate to 100 gallons of water, and after squeezing, passed for half an hour in a bath containing 8 gallons of sodium bisulfite (32° Tw.) in 100 gallons of water. It is finally washed, and boiled with a weak soap solution containing a blue color for tinting.[5]

A method of bleaching jute refuse of various origins for the preparation of paper stock is the following: The jute is boiled for 10 hours with 15 percent of lime and under a pressure of 1½ atmospheres, then washed and hydroextracted. The material is then exposed for 24 hours in a chamber to the action of chlorine gas, for which purpose for 100 lbs. of jute there are required 75 lbs. hydrochloric acid (20° Bé.) and 20 lbs. manganese dioxide, which corresponds approximately to 12 lbs. of chlorine gas.[6] The jute is then treated with a solution of caustic soda containing 1 lb. per 100 lbs. of jute. At a moderate temperature this dissolves the majority of the oxidized coloring matter. The jute is next washed and placed in a bleaching bath containing 5 to 7 lbs. of chloride of lime per 100 lbs. of material.

[4] Busch, *Jour. Soc. Dyers & Col*, 1901, p. 177.

[5] It is not possible to bleach jute a thorough white by treatment alone with chloride of lime, but by following this treatment with one with potassium permanganate it is possible to produce a full white. A good half-bleach on jute may be obtained by the use of the permanganate bleach alone.

[6] At the present time liquefied chlorine can be used as the source instead of the antiquated process of liberating it from hydrochloric acid and manganese dioxide.

3. **Bleaching of Hemp.**

Hemp is mostly employed for rope making, and is seldom used for the manufacture of woven fabrics, on which account it is seldom bleached except in a partial manner. When such a bleach is desired on hemp, the material is boiled for ½ an hour in a solution containing 10 kilos. sodium silicate per 500 liters of water. It is next boiled in plain water, then rinsed, and steeped for 24 hours in a solution of bleaching powder at 1° Tw. After this it is allowed to drain, and is then soured in hydrochloric acid at 1° Tw. It is finally well washed with water to remove the acid. If a lighter color is desired these operations are repeated several times.

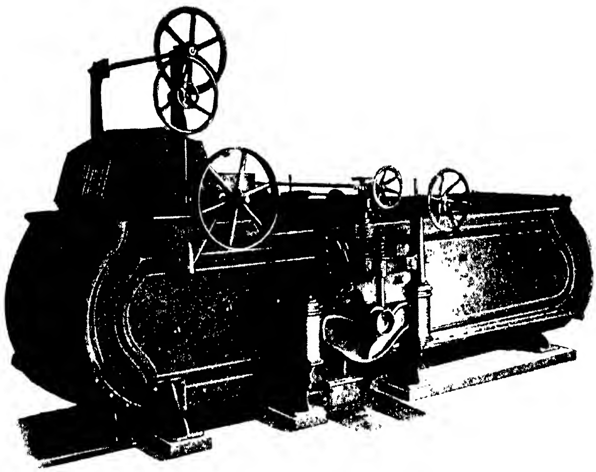

FIG. 290.—Miller Duplex Beater for Bleaching and Washing Paper Pulp.

Kapff and Stirm give the following process for the bleaching of hemp: The goods are first steeped in a weak acid bath and then boiled-out with soda ash without pressure; then wash, sour, wash, and chemic. For the latter purpose it is recommended to use an electrolytic hypochlorite solution; then rinse, sour and wash well. The hemp should then be of a light cream color; if a full white bleach is desired the process must be repeated a second time, using weaker boiling-out and chemic baths. Finally treat with a weak solution of soda ash, soap and treat with ultramarine. The fiber should now be a pure white and will show a loss in weight of 10 to 12 percent and a decrease in strength of 10 to 20 percent. The extent of these losses depends on the care exercised in the operations, as well as in the quality and condition of the hemp, its preparation and the strength and twist of the yarn.

Manila hemp may be decolorized to a considerable extent by boiling in a 5 percent solution of caustic soda for 2 to 3 hours, then washing

thoroughly and drying. The fiber does not appear to lose much in either its strength or its luster by this treatment, and the color is changed from a dark brown to a light yellow. Manila hemp may be further bleached to almost a pure white by steeping in a solution of sodium bisulfite (containing 1 part of sodium bisulfite liquor 20° Bé. to 10 parts of water) for 12 hours.

According to Carter, hemp yarns may be bleached as follows: (1) boil for 1 hour in a 10 percent solution of soda ash, wash and squeeze; (2) reel for 1 hour in a solution of bleaching powder of ½° Tw., and then wash thoroughly, or instead of reeling the yarn through the solution it may be steeped in the liquor for 10 to 12 hours; (3) sour for 1 hour in a solution of sulfuric acid at 1° Tw., and wash; (4) boil for 1 hour in a 2 to 5 percent solution of soda ash, and wash; (5) reel and wash as in (2); (6) sour again and wash as in (3). This will give a satisfactory half bleach.

4. Bleaching of Ramie.

When ramie (or China grass) has been properly degummed it bleaches rather easily and yields a white lustrous fiber of great strength and durability. The following process has been recommended for the bleaching of this fiber: (1) kier-boil in a dilute solution (0.3 percent) of soda ash, (2) chemic with a solution of sodium hypochlorite of 1° Tw., (3) sour with sulfuric acid of 1° Tw., and wash thoroughly. Ramie may also be bleached by the permanganate method, the fiber being steeped for 1 to 2 hours in a bath containing 1 percent of potassium permanganate; then rinse and immediately treat with a solution of sodium bisulfite in order to remove the brown deposit of hydrated manganese oxide. The permanganate method of bleaching ramie has also been used in conjunction with hydrogen peroxide.[7] In this process, after treatment with permanganate, a 2 percent solution of hydrogen peroxide is slowly added to the same bath in amount sufficient to decolorize the solution, the fiber being well worked in this bath in the meanwhile. This reaction results in the decomposition of both the permanganate and the peroxide.[8] Sufficient sulfuric acid should be present with the permanganate to prevent precipitation of manganic hydrate, as in the absence of acid the solution becomes alkaline owing to the production of caustic potash and manganic hydrate is formed.[9]

5. Bleaching of Artificial Silk.

This fiber consists of a form of cellulose (being a fine filament spun from a solution of cellulose) and consequently is bleached much after the manner of cotton. As the fiber, however, in its manufactured condition is very pure it does not require a previous boiling-out operation, and only requires a treatment with a hypochlorite or peroxide for the purpose of giving a white color.

There are three forms of artificial silk at present to be met with on

[7] Patent of McIvor and Chester.

[8] According to the following reaction:
$$5H_2O_2 + K_2Mn_2O_8 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$$

[9] $4H_2O_2 + K_2Mn_2O_8 = Mn_2(OH)_6 + 2KOH + 4O_2$.

the market: (1) *Chardonnet* or *nitro silk* made from a solution of nitrated cotton in alcohol-ether; this is also called *collodion silk;* (2) *cuprate silk* or *glanzstoff,* made from a solution of cellulose in cuprammonium hydrate; (3) *viscose silk* made from a solution of cellulose xanthate known as viscose.[10]

All these forms of artificial silk have the disadvantage of becoming much weakened on being wetted with water; consequently in the bleaching baths they must be handled with particular care and skill in order to obtain a satisfactory product.

The color of the crude or raw product is a pale yellowish white, and, though usually of a sufficiently good color for the dyeing of even pale shades, when used for white goods the fiber must generally be bleached.

Cuprate silk is probably the easiest to bleach. The silk is wetted out in lukewarm water and then put into a clear solution of bleaching powder at 2° Tw. and at 85° F. for half an hour. The goods are then rinsed in water and soured in a bath containing 5 percent (on the weight

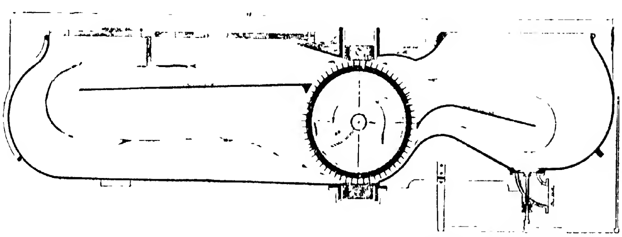

FIG. [illegible].—Diagram Showing Operation of Miller Duplex Beater.

of the goods) of sulfuric acid at 85° F. A thorough washing is then given to remove all the acid residues from the fiber which would otherwise tender the goods on drying. Finally, the silk is put through an antichlor bath containing 3 percent of sodium hyposulfite. A 5 percent solution of hydrogen peroxide can also be used for the same purpose. If a blue tone of white is desired the bleached material may be tinted with a small quantity of Alkali Violet or Acid Violet in a cold or lukewarm bath with the addition of 2 to 5 percent of acetic acid. Methyl Violet or Victoria Blue should not be used as the artificial silk takes up the color so rapidly that uneven tinting generally results.

Chardonnet silk is harder to bleach than cuprate silk, as it is more resistant to the action of the hypochlorite solution. It is customary to give this silk a preliminary treatment in a bath containing 10 percent of hydrochloric acid. It is rinsed thoroughly and bleached in a bath of bleaching powder solution at 2° Tw. at 85° F. for half an hour. The silk is then rinsed and put back into the hydrochloric acid bath, again rinsed, treated with an antichlor bath as above described, and finally tinted, if necessary, with Alkali Violet. If a soft handle is

[10] There is also a fourth form of artificial silk known as *acetate silk* and made from a solution of cellulose acetate. It has not as yet, however, met with any considerable degree of commercial success.

desired on the finished goods, 1 to 2 percent of olive oil previously emulsified with a little soda ash is added to the tinting bath.

In all the baths employed for tinting artificial silk, the amount of liquor should be about 50 times the amount of the silk; that is to say a 50-pound lot of silk will require 300 gallons of liquid.

Instead of using a solution of bleaching powder (chloride of lime) for the bleaching of artificial silk, a solution of sodium hypochlorite may be used, and perhaps with better advantage, as in the latter case there will be no insoluble lime salts to be removed from the fiber, and hence less washing and acid treatment will be required. The sodium hypochlorite solution may be prepared in the usual manner by taking 100 pounds of bleaching powder and stirring it up with 100 gallons of water. Allow the sediment to settle and draw off the clear liquor, which should stand at about 12° to 13° Tw. This solution consists principally of calcium hypochlorite and chloride with a small quantity of free calcium hydrate. A solution of 60 pounds of soda ash in 50 gallons of water are then mixed with the chloride of lime solution, the whole well stirred up and then allowed to settle. The clear liquor is drawn off and consists of a solution of sodium hypochlorite with a small amount of caustic soda. As it is best not to use an alkaline liquor for bleaching artificial silk, this solution should be carefully neutralized before using by the addition of the requisite amount of hydrochloric acid.

Another more convenient method for the preparation of sodium hypochlorite for the bleaching of artificial silk is by the use of a liquid chlorine. This is obtained as a liquefied gas under pressure in steel cylinders, and is utilized by passing the chlorine gas into a solution of caustic soda. By using the proper proportions a practically neutral solution of sodium hypochlorite is obtained. For 100 gallons of liquor use 48 pounds of caustic soda (76°) and 40 pounds of chlorine. The solution is tested with a few drops of phenolphthalein reagent and if not neutral more chlorine gas is passed in. Soda ash can also be used for the preparation of sodium hypochlorite from liquid chlorine, but as the solution in this case cannot be obtained neutral without decomposition its use is not recommended for the bleaching of artificial silk, as the considerable excess of alkali needed in the solution has a bad action on the silk.

6. Bleaching of Straw.

This material is very extensively used for the making of hats and passementerie and a great deal of the material is required to be bleached Straw is a cellulose vegetable material and consists of the stalks of various cereal plants or grasses. These are braided into plaits which are used for hat-making. Chip plait made from strips of willow or poplar wood is also used. Straw plaits are usually of a light yellow color which may be more or less pronounced, depending on the origin of the straw and the treatment it has been subjected to. The external surface of straw is also coated with a hard siliceous skin which is quite resistant to the penetration of solutions. In this respect straw differs

quite materially from chip plait, which is simply a thin cut tissue or strip of wood. Although the yellow color of natural straw may be quite satisfactorily bleached by the proper application of the several bleaching agents ordinarily used for bleaching the vegetable fibers, it does not appear to be possible to obtain a bleached white color that is at all permanent to exposure to the atmosphere, as the substance of the straw itself is gradually changed to a yellow color under the influence of sunlight and air.

Straw may be bleached by either the sulfurous acid or the peroxide method. The former is carried out in the same manner as for wool, the straw being exposed to the action of the sulfurous acid fumes for several hours. As a rule, the finer the straw, the longer will be the time required for the bleaching. When bleached by the sulfurous acid

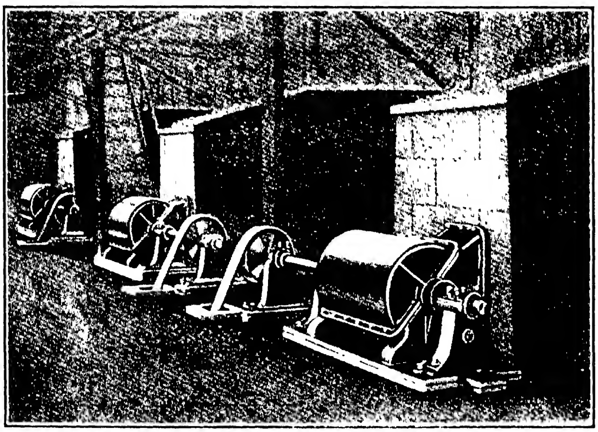

Fig. 292. Bellmer Bleach Tanks for Paper Pulp

process, however, the straw is liable to regain its yellow color on exposure, especially to sunlight. The peroxide bleach is carried out in the usual manner with the use of sodium peroxide, and appears to be eminently suited for straw, as the bleach is more permanent. Chloride of lime has also been used for the bleaching of straw, the goods being previously boiled in a bath of dilute caustic soda. The bleach liquor should stand at about 1° to 2° Tw., and the straw is subsequently washed in dilute hydrochloric acid, and then in several changes of fresh water in order to remove all trace of acid.

In order to prepare straw plait for bleaching it is first soaked for several hours in hot water in order to soften the fiber. It may also be steeped in a hot solution of sodium silicate, though it is necessary to avoid too severe action with hot alkaline liquids as this tends to dissolve off the siliceous structure, causing the straw to become weak and brittle and to lose its luster. After a thorough wetting-out the straw is steeped

for several hours in a lukewarm bath (120° to 140° F.) containing hydrogen peroxide (1 to 3 percent). This may be prepared either from the commercial hydrogen peroxide solution or from sodium peroxide in the manner given on page 137. After treatment in the peroxide bath a rinse should be given in a solution of oxalic acid and tartar, 4 pounds of each being used to 100 pounds of straw plait.

The following method is an Italian process for the bleaching of straw, and though it is rather long and tedious, it is said to give excellent results:

(1) Soak the straw in water overnight, and dry.

(2) Place the straw in a bath of 100 gallons of water and 15 gallons of hydrogen peroxide, and about 10 lbs. of water glass. Enter the material at about 175° F, and keep at that temperature, for 12 to 16 hours, after which rinse and dry.

(3) The straw is next placed in a strong solution of sodium bisulfite for 12 hours.

(4) The straw is rinsed and dried, and placed in a cold bath containing 4 lbs. of acid potassium oxalate and 8 lbs. of sodium bicarbonate for every 100 gallons of water. After 12 hours, rinse, sulfur for 7 to 8 hours, and dry.

(5) A final cold bath is given, containing 5 lbs. of acid potassium oxalate and 4 lbs. of sodium bicarbonate for every 100 gallons of water, and followed by a repetition of the sulfuring.

Good results are also said to be obtained by the following simple method: Soak the straw overnight in cold water, and give a cold bath of 100 gallons water, 16 lbs. of oxalic acid, 10 lbs. sodium peroxide, and 10 to 15 lbs. of sodium silicate. After 10 to 12 hours the bath is warmed. The straw is then rinsed, sulfured, rinsed, and dried.

A German process for the bleaching of straw is to soak the material for 3 hours in warm water, and then a solution of soda ash at 120° F., after which they are placed in a bath containing 1 lb. of chloride of lime for each 25 lbs. of straw. The material is left in this bleaching bath for 1 hour, after which time a small quantity of dilute hydrochloric acid is added, and the straw is left for half an hour longer. After this treatment the straw is washed at first in a one percent solution of soda ash, and then in fresh water. It is also said that the characteristic luster often exhibited by straw may be removed by treating with a bath containing one percent of picric acid.

The older method of bleaching straw was with the use of sulfurous acid gas (fumes from burning sulfur). The old Luton bleach which was long successfully practised in England was as follows:[11] For 100 pounds of straw plait first steep overnight in cold water, then wash in a warm bath of soap and soda ash; rinse and work in a bath containing 4 pounds of oxalic acid and 4 pounds of tartar and 4 pounds potassium carbonate until the yellow color has largely disappeared. Rinse well and expose in the sulfur chamber, repeating if necessary a second time to obtain a satisfactory bleach.

The peroxide method of bleaching, however, has largely superseded the sulfur bleach, though often the two methods are combined in order to produce a fine color.

[11] R. B. Brown, *Jour. Soc. Dyers & Col.*, 1899, p. 28

Chip plait is bleached by practically the same methods as those employed for straw. In order to produce the desired results and at the same time to preserve the luster and natural qualities of the material a good deal of art has to be practised in addition to the conventional methods of bleaching, and this can only be learned in the practical working of the material.

According to the Badische Co.[12] straw may be bleached by hydrosulfites in the following manner: A solution is prepared containing 1 kilo. of powdered sodium hydrosulfite, 500 grams of crystallized sodium phosphate, 300 grams of soda ash and 100 liters of cold water. The

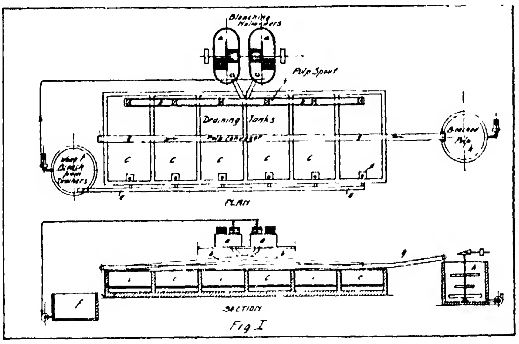

Fig. 293.—Tank System of Bleaching Paper Pulp.

straw is placed in this bath and then the temperature of the liquor is gradually raised to 60° to 70° C., and is maintained at this point for about 12 hours, when it is slowly allowed to cool. The goods are then removed from the bath, thoroughly washed and further treated for 2 to 3 hours in a bath containing 2 grams of oxalic acid per liter at a temperature of 30° to 40° C. Then finally wash and dry.

7. Bleaching of Paper Pulp.

This material is composed of vegetable fibers derived from wood, cotton, linen, straw or other sources. It is bleached by the use of hypochlorite solutions, the principal agent used being bleaching powder or chloride of lime. In fact the principal and largest use of bleaching powder is for this purpose. Paper pulp when mixed with water forms a broth of a semi-liquid consistency; the fiber is beaten up with water in an apparatus known as a beater which keeps the material in continual suspension and circulation and allows of a very thorough and intimate mixing. The bleaching powder (either in the dry powder form or as a concentrated solution) is added directly to the pulp mass in the beater, and the latter is run for a couple of hours, or until the fiber is satisfactorily bleached. The material is then washed and soured with a solution of about 4 pounds of sulfuric acid in 16 pounds of water for

[12] Fr. Pat. 420,725.

each 100 pounds of bleaching powder used. After the sour treatment the white color is much enhanced and the full action of the bleach is developed. The pulp is then well washed and usually treated with a small quantity of antichlor (sodium bisulfite or sodium thiosulfate) in order to destroy or neutralize the last traces of chlorine compounds.

Another method of operating in the bleaching of paper pulp is to run a continuous system; the fluid pulp is run into a high cylindrical wooden tank where it is mixed with the required bleaching solution and suitably mixed by a revolving agitator. The pulp and the bleach liquor run in continuously in the proper proportion and as the first tank fills up it overflows from a bottom outlet into a second similar tank where the treatment and agitation is continued. A battery of six to ten tanks may be used in this manner with a regulated progression of the pulp so that when the last tank is reached the bleaching of the pulp is completed.

Large pulp mills use such an amount of bleach that frequently an electrolytic installation is employed, for the production of chlorine on the one hand and caustic soda on the other. The latter is used in the cooking of the wood to produce the fiber, while the chlorine is absorbed in milk of lime or caustic slaked lime to produce bleaching powder. Instead of using chloride of lime it is possible to also use sodium hypochlorite by absorbing the chlorine gas in a solution of caustic soda until a neutral bleach liquor is obtained. It is not well to use an alkaline bleach liquor for wood pulp as the liquor in the pulp is discolored by the alkali.[13]

It is also possible to use the chlorine for bleaching by properly absorbing it in water containing a small amount of alkali, and using this solution for bleaching the pulp. By employing a suitable device for feeding in the chlorine and mixing it with the water a continuous bleaching process may be used or the chlorine solution may be fed directly into the pulp in the beater in the usual way.[14]

The amount of chloride of lime required for bleaching paper pulp

[13] According to Ebert (*Papierfabr.*, 1911, p. 305) who describes a typical Siemens-Halske installation of cells, the concentration of the caustic soda liquor at the cathode is about 130 grams per liter. A unit consuming about 10 HP. produces in 24 hours about 57 kilos. of chlorine gas and 64.4 kilos of caustic soda. In actual practice, the production of 1 kilo. of active chlorine in the form of bleaching liquor requires a current of about 4 KW hours, as against 6 KW hours in the production of a corresponding amount of electrolytic bleach liquor. The consumption of salt depends on the manner in which the caustic soda is utilized; if the liquor can be used directly as it comes from the electrolyzers and containing a certain proportion of salt, the costs of evaporation and purification are eliminated, but the consumption of salt is about 3 kilos per kilo. of active chlorine. If the soda lye is concentrated and purified, the salt is recovered and the consumption then falls to about 1.6 kilos. These figures compare with a corresponding salt consumption of 5 kilos. for the preparation of electrolytic hypochlorite.

[14] An interesting comparison between the efficiency of bleaching powder and electrolytic hypochlorite in the bleaching of rag pulps for paper is given by Fraass (*Papierfabrikant*, 1910, p. 62). The concentration of the pulp used was 5 percent and the charge of each engine was 330 kilos of dry fiber substance. The electrolytic liquor was slightly alkaline, but in all cases hydrochloric acid was added to the pulp during bleaching. The following results indicate the economy effected by the use of the electrolytic liquor: cotton-linen union rags; (a) bleaching powder, 4.29 kilos. of active chlorine, 1050 c.c. of hydrochloric acid; (b) electrolytic liquor, 3.148 kilos. of active chlorine, 700 c.c. of acid. Light printed calicoes, (a) bleaching powder, 3.387 kilos of active chlorine, 800 c.c. of acid; (b) electrolytic liquor, 2.032 kilos. of active chlorine, 700 c.c. of acid. It was remarked that in all cases the electrolytic liquor gave brighter colors than the bleaching powder, and also gave a softer fiber. The duration of the bleaching process was always the same. The electrolytic bleach was characterized by a relatively rapid start, then the color changed more slowly than with the bleaching powder solution, but later the electrolytic solution regained headway and the final result was superior.

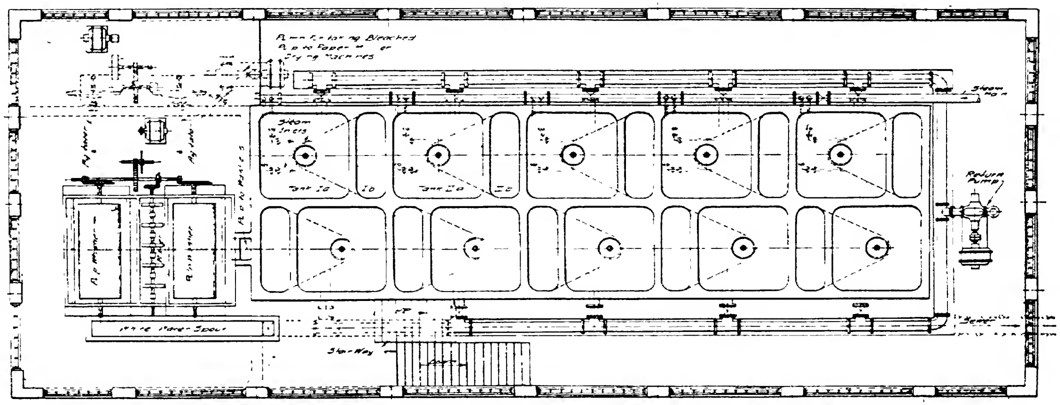

Fig. 294—Continuous Tank System of Bleaching Paper Pulp (Plan).

corresponding degree of whiteness. These pulps are washed by shaking twice with successive quantities of 1 liter of water, and drained by suction. In order to prepare sheets of them for record, each lot of bleached pulp is shaken with 500 cc. of water and poured into a porcelain filter-pump funnel, the perforations being covered with a fine wire gauze. The stem of the funnel is provided with a tap so that the whole of the fluid pulp may be distributed evenly before any of the liquid runs through. The sheets so formed are placed between filter-paper and passed through a wringing machine and dried in the air, then strips from each are mounted on a frame of black cardboard so arranged that they may be compared by transmitted as well as by reflected light.

8. Bleaching of Leather.

The production of bleached or white leather has rather to do with the process of tanning or tawing whereby the raw hide is converted into a leather rather than with a distinctive process of bleaching the prepared leather itself. It is hardly possible to bleach ordinary leather as prepared by either the vegetable or chrome tannage; in the one case a brown colored leather is obtained, while in the latter case a greenish colored leather is produced.

White leather, however, is largely made from light-weight hides, such as goat (kid) and sheepskins, for use in the manufacture of gloves, shoe-tops and fancy leather articles. Leather for this purpose is tanned by the alum or oil process, and finished with an egg-yolk or oil emulsion.

9. Bleaching of Bone.

Bone is an animal tissue combined with a skeleton of mineral matter, and it is used in the manufacture of a variety of articles, such as buttons, toilet articles and various fancy goods. In the bleaching of bone the material should first be boiled for 2 to 4 hours in a dilute solution of salt and soda ash for the purpose of removing particles of flesh, marrow and sinew. It is then well rinsed in water and bleached with a solution of sodium bisulfite, bleaching powder or hydrogen peroxide. Bone material intended for use as piano keys may be bleached by steeping in running water for 10 to 12 weeks, and then after-treating with a solution of sulfurous acid. The latter reagent should never be used in the gaseous state on the bone material as the bone will develop cracks.

Bone may be bleached with chloride of lime by using a solution containing 1 part of bleaching powder to 4 parts of water. The well-cleaned bones are steeped in this solution for several days and then rinsed well and dried.

According to Hedriger bones may be bleached by steeping in turpentine for 10 hours in a tightly closed iron drum. The goods are then boiled for 3 hours in a dilute soap solution, rinsed in water and dried on wooden shelves without exposure to the sun; a good white is developed in the course of a few days.

According to Augenstein the bones are boiled in a concentrated solution of alum for an hour and then thoroughly brushed, after which they are gradually dried in damp sawdust to prevent cracking.

A very good white on bone material is said to be obtained by steeping in hot turpentine for 10 to 12 hours, then boiling in soap-boilers' lye, and finally exposing to the sun for several days.

Bones may best be bleached, perhaps, by the use of hydrogen peroxide. The material should first be dipped in gasoline or solvent naphtha; then wiped well with a cloth and then steeped in a ½ percent solution of hydrogen peroxide until the desired degree of whiteness is achieved. To obtain a good white product it is necessary to start with as fresh a bone as possible; old bones are very difficult to bleach in a satisfactory manner.

10. Bleaching of Ivory.

This material is only bleached when old stock is used that has become yellow in color; new ivory is seldom, if ever, bleached. In the bleaching of ivory articles practically the same procedure is carried out as with bone. Solutions of hydrogen peroxide are principally used as the use of such chemicals as sulfurous acid, sodium bisulfite or chloride of lime tends to cause decomposition of the cell structure of the ivory and also seriously deteriorates the luster. The ivory is simply steeped in a ½ to 1 percent solution of hydrogen peroxide made slightly alkaline with ammonia and kept at a temperature of about 120° F. for several hours, or until a satisfactory white color is obtained. Before bleaching the ivory should be well scoured with warm soap and rinsed; or better yet, first dip the dry ivory in benzine or solvent naphtha to remove the grease, then rub off well with a woolen cloth and then scour in a warm soap solution. After bleaching in the peroxide bath the ivory may be somewhat improved in color by dipping in a dilute (5 grams per liter) solution of oxalic acid, then rinsing well by steeping in running lukewarm (120° F.) water. In drying the ivory should not be heated too rapidly as it is liable to crack and split. It is best dried slowly at a low temperature. The surface should also be polished by working in damp sawdust or by other suitable means.

11. Bleaching of Horn.

Horn is a substance employed for buttons and small ornamental articles in a manner very similar to bone and ivory. Most qualities of horn are colored brown or gray from natural pigments and generally the color is quite dark. This pigment penetrates entirely through the material, and owing to the hard, resistant character of the horn substance it is not possible to bleach it out with any degree of satisfaction. Furthermore, the horn tissue is quite easily affected by chemical agents, and any severe chemical treatment which would at all effectively bleach out the pigment would seriously injure the horn itself.

The bleaching of horn is really not a process of destroying or removing the natural pigment as is customary in most bleaching operations, but is simply done by impregnating the horn tissue with a white pigment so that the horn acquires a milky white opalescent appearance. It is really dyeing the horn white, and the process is carried out as

follows: The horn is first stained brown with red lead and then dipped in dilute hydrochloric acid, whereby the lead sulfide at first formed in the substance of the horn is converted into white lead chloride. The lead stain is made by stirring 5 pounds of caustic lime and 3 pounds of red lead with a solution of caustic potash. The horn must not remain in this solution too long as it will become brittle. The hydrochloric acid used for the dipping should be very pure and free from arsenic and iron, otherwise the white color will not be satisfactory.

12. Bleaching of Feathers.

Feathers consist of animal tissue very similar in chemical constitution and properties to wool and the other animal fibers. The processing of feathers, however, is complicated by the fact that the feather as a whole must be more or less treated as a unit, and in the feather there are two distinct parts, the fine, fibrous fronds and the stiff horny tissue of the quill with its radiating branches. These two portions of the feather, being so different in their physical make-up, are very differently affected by chemical solutions; consequently great skill and care must be exercised in the treatment of feathers.

Feathers also differ widely in their quality, depending on their origin. Some are stiff and highly colored, while others are soft and downy, and in some cases practically white. The highly colored feathers are not bleached, this process being limited to the so-called white feathers and more especially to ostrich plumes.

Like wool, feathers are coated with considerable grease and oil, and before they can be bleached this greasy coating must be removed. This is usually done by soaking the feathers in benzine or solvent naphtha for several hours, using a closed vessel to avoid waste of solvent. Some form of agitation should be provided in order to move either the fluid or the feathers so as to facilitate the solution of the grease. The feathers, however, should not be agitated with any violence, as otherwise the sprays will become matted and crushed. After cleaning the material should be slowly dried in a gentle current of warm air at about 160° F.

The bleaching is done by steeping the feathers in a 1 to 3 percent solution of hydrogen peroxide with the addition of sufficient ammonia to give a slight alkaline reaction with red litmus paper (turning it blue). The feathers should be loosely tied in small bundles and immersed completely beneath the surface of the liquid. If a cold bleach bath is used it will require from 10 to 60 hours to obtain a satisfactory color; but by heating the bath to 100° to 120° F. the time for bleaching may be materially reduced. It is also well to have some means of gently circulating the liquid, either by working the feathers about in the bath or by suitable mechanical means.

After the bleaching treatment is finished the feathers must be well rinsed in plenty of soft water, and preferably in the first rinse water a small amount of oxalic acid may be used. After rinsing, the feathers are usually steeped in a bath of alcohol (sometimes with the addition of 10 percent of ether). The goods are then centrifuged by whirring on a

special apparatus for this purpose. When the feathers are dry they are dipped several times in clean benzine and then dried by waving in the air or by placing in a warm vacuum chamber. The fronds are then curled by working over a knife edge.

When old and worn feathers are to be cleaned and bleached it is customary to first treat them with a clean soap solution. The latter may be prepared by boiling 3 ounces of good white tallow soap in one gallon of pure soft water; skim off any insoluble matter and let the solution cool. The feathers are first soaked in lukewarm soft water for some time in order to thoroughly soften and wet them out. The feathers are then spread out on a smooth board and scoured with the soap solution by means of a soft pad of cloth. After scouring the goods are rinsed well in lukewarm water, and then spread out and pressed gently between clean dry cloths, at the same time heating the feathers gently with the hand. When the feathers are nearly dry they may be bleached as above described by steeping in a solution of hydrogen peroxide made slightly alkaline with ammonia.

Feathers may also be bleached in a manner very similar to the stoving of wool by subjecting the moist and clean material to the action of sulfurous acid gas (fumes of burning sulfur) or by steeping in a solution of sodium bisulfite. This is the older process of bleaching, but it has now been practically superseded by the peroxide method which is much more convenient in its method of application and which also gives more satisfactory results.

Hydrosulfite compounds have also been used for bleaching feathers, but the results obtained are not so satisfactory as with the peroxide method.

Feathers may also be bleached by the use of potassium permanganate; well cleansed goods are steeped in a solution of this salt containing 5 to 10 grams per liter. The solution is used cold and for about ½ hour. It is also well to add a small quantity of sulfuric acid to the permanganate solution in order to prevent the formation of a brown precipitate. After this treatment the feathers will be colored a deep brown, due to formation of a hydrated oxide of manganese. In order to remove this the goods are rinsed off in fresh water and then steeped in a solution of sodium bisulfite (5° Tw.) at 120° F. until the brown stain is all removed; the bleaching effect of the permanganate will then be seen. A thorough rinsing should then be given in order to remove all trace of the bisulfite liquor.

Bleached feathers may be tinted if desired to a bluish tone of white by the use of various blue or violet coloring matters. The chief tints used are Victoria Blue, Methyl Violet, Acid Violet, Indigo in fine suspension or Indigo Extract.

13. Bleaching of Sponges.

At the present time sponges are quite extensively bleached, the purpose being to reduce the rather dark brown color of the natural sponge to a pale yellowish brown color. Sponge is a peculiar fibrous material which is contaminated with considerable soluble material derived from

the evaporation of the salt water, and also it contains considerable calcareous matter in the cell tissue.

For the bleaching of sponge the material should first be steeped for several days in a number of changes of fresh water in order to remove all soluble matters. To remove the lime or calcareous matters, the sponges are then steeped in a cold 5 percent solution of hydrochloric acid for several hours, and after this the goods should be thoroughly rinsed in several baths of fresh water. The bleaching may then be accomplished by steeping the sponge in a solution of sulfurous acid or sodium bisulfite of 8° Tw. strength. The treatment is repeated several times until the color is satisfactory. The goods are then rinsed for 24 hours in several changes of fresh water.

Bleaching may also be done by the use of hydrogen peroxide, using a solution of 1 to 3 percent strength made slightly alkaline with ammonia, the goods being simply steeped in the peroxide solution until the color has been sufficiently bleached.

Sponges may also be bleached by the use of potassium permanganate in the usual manner. The goods are steeped for ½ hour in a solution of potassium permanganate containing 5 to 10 grams per liter. Before bleaching, of course, the sponges should be thoroughly cleaned, the calcareous matter being removed by treatment with dilute muriatic acid as above described. After coming from the bath of potassium permanganate the sponges exhibit a dark brown color, due to the formation of an oxide of manganese. This is removed by steeping the goods in a cold solution of sodium bisulfite at 50° Tw. until all the brown deposit is dissolved. Afterwards a thorough rinsing should be given to remove all residues of chemicals.

Sponges after bleaching are generally tinted with a yellow dyestuff, for which purpose Phosphine and Auramine are generally employed.

Chapter XXVI.

Stripping of Dyed Colors.

1. General Remarks.

The stripping of dyed colors has to do with the removal of dyes from various textile materials, either for the purpose of correcting an over-dyed shade or for obtaining a lighter colored bottom for the re-dyeing of another color. There is a large amount of dyed material spoiled in the mill, either on account of getting off shade or becoming uneven or spotted. Frequently this is turned into black, but sometimes it may be desirable to strip off the color in order that the goods may be re-dyed either to the same original color in case of unevenness, or to a lighter color. The fashionable colors for different seasons change from time to time, and there may be quite a saving realized if the old colors of left-over stock can be removed or stripped sufficiently to allow of being re-dyed to the more acceptable shades.

Another class of material subjected to the stripping process very frequently is shoddy or worked-over woolen material. As this is derived from all manner of rags, clippings, etc., there will occur in it a large amount of colored material of all manner of shades. Shoddy is usually carefully sorted into several grades for color, that is, the dark colors are placed together, then a lighter range of colors, and so on down to very light colors. In cases where the color is quite light, it may not pay to remove the dye and the goods are put into cloth which is dyed a shade sufficiently heavy to cover up the irregularities of color in the original stock. But with heavily colored stock, it is often necessary to strip off the color at least partially, in order to obtain material to be put into other colors than black, as in this manner the value of the stock is much enhanced.

Cotton is seldom stripped, except in cases where a color has become uneven or gone off shade, or in cases of garment dyeing and cleaning. More generally, however, cotton material, if to be re-dyed is either dyed in a darker color capable of going over the original color, or is turned into black. When it is required to strip cotton rags this is usually done by boiling with a solution of soda either with or without an after-treatment with hydrosulfite solutions.

Although the principles of stripping are in general about the same as those in ordinary bleaching, the conditions are necessarily somewhat different, for in stripping we have to deal with coloring matters other than those naturally present in the fibers themselves; and also, it must be borne in mind that the dyes dealt with belong perhaps to many different classes, and occur in much larger amount than the

natural color of the fiber. The methods of stripping will in a great extent be conditioned by the kind of fiber or material being dealt with, and in the second place with the character of the coloring matter which it is desired to remove, and the depth of the shade together with the character of the color it is desired subsequently to place on the goods.

The effect of the principal stripping agents on the cotton and wool fibers is as follows:

Stripping Agent	Cotton	Wool
Soda ash.	Little or no effect.	Liable to become brittle, harsh and rotten if process is not carefully regulated.
Hydrosulfite formaldehyde compounds	Little or no effect.	Slight tendering and considerable loss in weight occur.
Sulfuric acid	Must be well washed out or cotton will be tendered in dyeing.	Unless in great excess has little or no effect.
Bichromate	Tenders only if used in excess.	Is far more active than sulfuric acid in tendering.

2. Stripping of Woolen Goods.

The method to be employed for the stripping of woolen goods will depend to a considerable degree on the nature of the dyestuff on the material.

The effect of different stripping agents on the colors of woolen rags is as follows:

Stripping Agent	Color of Rags	Color stripped to
Soda ash-hydrosulfite reagent	Blues Browns Greens Reds	Bluish gray Light green Light bluish gray Light pinkish drab
Bichromate of soda (8 percent) and sulfuric acid (8 percent)	Blues Browns Greens Reds	Dark reddish slate Yellow orange Greenish drab Slightly browner

On gray and faded black rags the soda-hydrosulfite strip is not very effective, and consequently the bichromate-sulfuric acid strip is generally employed. This gives a reddish brown to a light drab color depending on the amounts of chemicals employed. The maximum percentage that can be used is 8 percent of sodium bichromate and 8½ percent of sulfuric acid as higher percentages cause a tendering of the fiber. A lighter strip can be obtained by subsequently giving a fresh

hydrosulfite bath, but this of course will increase the cost of the process.

For a light gray strip on blues and greens or a light drab on browns and reds use 4 percent of soda ash, though if the rags have been carbonized, it may be necessary to use up to 10 percent of alkali in order to neutralize the residual acid in the fiber. Start the goods at 120° F. and slowly bring up the temperature to 180° F., or until it is apparent from the feel of the goods that it is unsafe to proceed further. Allow to stand at least half an hour in the hot liquor and then wash off in two waters; then fill up the bath again and add 4 percent of Hyraldite Z (or similar hydrosulfite compound) or 8 percent of sodium bisulfite. Slowly bring to the boil and maintain at that temperature for half an hour. Under no circumstances should acid be added to the bath.[1]

To obtain a light drab on faded black rags boil the goods first for 5 minutes with 8 percent of sulfuric acid; run off the liquor, fill up with water and add 8 percent of sulfuric acid; boil for 20 minutes, run off the liquor, wash with water, fill up the bath again and add 3 percent of Hyraldite Z (or equivalent hydrosulfite compound) and gradually bring to the boil and maintain at that temperature for 20 minutes; then finally wash.[2] In order to cheapen the cost the hydrosulfite compound may be replaced by sodium bisulfite (6 percent), but the stripped color will be darker.

Hydrosulfite stripping is now displacing most other processes because it is the most generally effective and it leaves the wool fiber in the most satisfactory condition. A bath recommended for this purpose is

2 to 4 percent of Hyraldite Z (or similar hydrosulfite compound)
2 to 5 percent of Formic Acid (85 percent strength)

If formic acid is not available, one half the quantity of sulfuric acid may be used. The shoddy or rags is entered at 120° F. and the bath gradually brought to the boil and continued for half an hour at that temperature. After thorough rinsing and neutralizing the stripped material is ready for re-dyeing. Instead of employing the prepared bisulfite compounds the dyer may prepare his own stripping solution from sodium bisulfite and zinc dust as follows:

10 gallons of water
10 pounds of zinc dust
10 gallons of sodium bisulfite (70° Tw.)

The zinc dust is stirred in slowly, and then the solution is allowed to settle until it becomes clear. The stripping bath is then prepared as follows:

4 to 6 gallons of the above solution
5 pints of acetic acid
100 gallons of water

The material to be stripped is entered into this solution at 140° F. for 20 to 30 minutes. When the stripping is finished the material is washed, soured and washed again. This stripping solution consists of

[1] The cost of this method of stripping is about 1½ cents per pound.
[2] The cost for this method will be about 2 cents per pound.

a sodium hydrosulfite in admixture with sodium zinc sulfite and acts best when prepared fresh and added to the stripping bath just previous to being used.

3. **Stripping Acid Colors.**

The great majority of woolen goods which it is desirable to strip will be dyed with acid colors, and usually these dyes are more or less readily removed by means of alkaline baths. Solutions of ammonia are often quite efficient in stripping acid colors, though usually the removal of the color is by no means complete, yet sufficient dyestuff may be removed very frequently so as to bring the depth of the color down to a point where the goods are available for use in re-dyeing. This method of stripping is especially good where material has been dyed over the shade and it is only desired to lighten the color to some extent. There are, of course, acid dyes which are not amenable to this treatment, and are but little affected by even strong solutions of ammonia, applied either hot or cold. Solutions of sodium carbonate are also useful for the stripping of some acid dyes, but care must be had in the use thereof that the bath employed is not too strongly alkaline, as otherwise the wool itself may be seriously injured. Solutions of soda ash should not be used at temperatures above 180° F. in general practice; only coarse material of low value should be subjected to temperatures higher than this. Soap solutions may at times be employed for the stripping of acid colors with considerable success, and usually with less injury to the fiber than when soda ash is used, as the bath can be employed at a higher temperature without fear of injury to the material. Caustic soda should never be employed in an attempt to strip acid colors from woolen material, as this reagent will destroy the wool fiber.

Many acid dyes are stripped to a considerable extent by treatment with a boiling concentrated solution of glaubersalt, and in cases where it is simply the purpose to lighten an overdyed shade, this method of procedure is a very good one.

In cases where it is desired to decolorize the material to a greater extent than possible in the above methods, more severe treatments must be resorted to; as, for instance, when it is desired to strip dark colored shoddy so that it will take light colors on subsequent dyeing. One of the methods employed in such a case is a treatment with chromic acid; the latter usually being obtained from a mixture of potassium bichromate (or sodium bichromate) and sulfuric acid, or a mixture of the bichromate and oxalic acid. A bath is made consisting of 3 to 5 percent of chrome and 4 to 6 percent of sulfuric acid (on the weight of the material), and the goods are boiled therein for 15 to 45 minutes, and then washed thoroughly in warm water containing a little ammonia. Another form of the bath is to use 2 to 4 percent of chrome, 2 to 4 percent of oxalic acid, and 3 to 5 percent of sulfuric acid.[3] This method of stripping also causes a mordanting of the ma-

[3] The following method of stripping is said to give very good results; especially when used on carbonized rags: For 100 lbs. of carbonized rags treat with a bath containing 100 gallons of water, 2½ lbs. chrome, and 2½ lbs. sulfuric acid at 100° F., for 18 hours. Then rinse

terial with chrome, so that it may subsequently be dyed with alizarine colors immediately. Care must be had not to have the bath too strong with chrome, as the fiber itself may be oxidized, and thereby weakened in strength and altered in its dyeing properties.

A solution of sodium hydrosulfite may also be used to good advantage in the stripping of acid colors, especially on shoddy. The clear solution of freshly prepared hydrosulfite may be used in connection with a little acetic acid, or in the majority of cases simply a mixture of sodium bisulfite and zinc dust is made in the bath which is then brought to the boil, and the goods entered and worked until the color is sufficiently stripped; after which the goods are passed through a lukewarm bath containing a small quantity of hydrochloric acid for the purpose of removing any adhering particles of zinc; the goods are finally washed in fresh water. Sodium hydrosulfite and the prepared hydrosulfite-formaldehyde compounds will strip a great many acid colors almost completely, so that the goods will be left almost white.[4]

Some of the acid dyes may also be partially stripped by the use of sodium bisulfite solutions or sulfurous acid, in the manner practiced in the bleaching of wool; but the stripping is only partial, and it is difficult to remove the sulfurous acid from the wool, and also the color is liable to return after a time.

Stannous chloride and hydrochloric acid will remove many of the acid colors; some of them, in fact, being stripped almost completely.

Another efficient stripping agent is potassium permanganate followed by a treatment with sodium bisulfite; almost any class of color may be removed to a greater or lesser extent by this method.

4. Stripping Basic Colors.

As these dyes are not much used on wool, this condition will seldom arise. Hot soap solutions will generally remove a considerable part of the color; and in the case of some colors, weak acid baths may be used to advantage. Treatment with chrome and sulfuric acid or with sodium hydrosulfite as outlined above is also a good means of removing basic colors. Stannous chloride and hydrochloric acid may also be employed for the removal of basic colors, and in many cases is a very good method.

5. Stripping Alizarine and Mordant Colors.

These are as a rule rather difficult to strip to any degree of satisfaction; but the use of chrome and acid will give good results in many cases. Sodium hydrosulfite will also decolorize many of these dyes. The natural dyes are more easily stripped than the alizarines; Log-

well in water and pass through a bath of dilute sulfuric acid till all trace of the chrome has been removed. Next treat with another bath for 6 hours at 100° F., and containing 100 gallons of water, 9 lbs. magnesium sulfate, and 3¼ lbs of sodium peroxide, the magnesium sulfate being added first in the preparation of the bath. Rinse well and pass into a third bath prepared in the same manner as the second, and leave for 8 hours at 100° F. Rinse well in water acidulated with sulfuric acid, then in a weak soap bath, then in water It is said that the shade obtained on rags by this method is quite light and the process does not injure the fiber.

[4] The principal compounds of this class that are used as stripping agents are Hyraldite Z, Rongalite, Decroline and Hydrosulfite NFX, Burmol and Formosul

wood may be taken off with oxalic acid, and Indigo with a solution of chrome and sulfuric acid.

6. **Stripping Substantive Colors.**

As a rule these are rather difficult to remove; the best means being to use a bath of sodium hydrosulfite, though in some cases stannous chloride and hydrochloric acid work very well.

7. **Stripping of Cotton Goods.**

Dyed cotton material is not stripped except in cases where the dyeing has gone over the shade and it is desired to reduce the color partially. Where the substantive colors are used, considerable color may be removed by simply boiling in water or in a soap bath. Treatment with stannous chloride and hydrochloric acid will also remove many of these dyes almost completely. Sodium hydrosulfite may also be used. Solutions of chloride of lime or sodium hypochlorite are also very efficient stripping agents for all classes of colors on cotton. Oxalic acid may be used for stripping Logwood, and Indigo is removed by treatment with chrome and sulfuric acid as in the case of wool. Basic colors are rather easily stripped; some will lose a large amount of color by boiling in a solution of soap, while others may be removed with stannous chloride or sodium hydrosulfite. The sulfur dyes may be stripped more or less with chloride of lime. Cotton material, such as curtains, drapery, etc., which has been dyed with acid colors, may generally be stripped satisfactorily by simply boiling in a solution of soap, or in a bath containing both soap and soda ash.

Iron Buff on cotton may be stripped by boiling in a moderately strong solution of oxalic acid; khaki shades dyed with chromium and iron salts may also be stripped in the same manner. If the latter, however, are bottomed with Cachou de Laval or other sulfur dyes, this treatment will only remove the metallic color, and the other dyestuff must be removed by subsequent bleaching.

Perhaps the best method for discharging basic colors, however well mordanted they may be, is to boil the cotton in a moderately strong solution of caustic soda, with or without the addition of soap. The same treatment will also decolorize Chrome Yellow and Chrome Orange. Slates and drabs obtained from iron salts and tannin are easily stripped by a treatment with warm dilute solutions of mineral acids, or even oxalic acid. Logwood blacks may be discharged by the same treatment down to a light brown. Aniline Black cannot be stripped satisfactorily by any reasonable treatment.

For the stripping of diazotized colors, Bonnet recommends that the material be dampened and then dipped in a one-tenth percent solution of potassium permanganate, whereby a thin layer of manganese peroxide is precipitated on the fiber; a weak bath of hydrochloric acid (1 part of acid to 5,000 of water) is then given, which results in the generation of a small amount of chlorine in the fiber through the reaction between the peroxide of manganese and the hydrochloric acid. The chlorine thus generated is said to destroy the color without injuring the

terial with chrome, so that it may subsequently be dyed with alizarine colors immediately. Care must be had not to have the bath too strong with chrome, as the fiber itself may be oxidized, and thereby weakened in strength and altered in its dyeing properties.

A solution of sodium hydrosulfite may also be used to good advantage in the stripping of acid colors, especially on shoddy. The clear solution of freshly prepared hydrosulfite may be used in connection with a little acetic acid, or in the majority of cases simply a mixture of sodium bisulfite and zinc dust is made in the bath which is then brought to the boil, and the goods entered and worked until the color is sufficiently stripped; after which the goods are passed through a lukewarm bath containing a small quantity of hydrochloric acid for the purpose of removing any adhering particles of zinc; the goods are finally washed in fresh water. Sodium hydrosulfite and the prepared hydrosulfite-formaldehyde compounds will strip a great many acid colors almost completely, so that the goods will be left almost white.[4]

Some of the acid dyes may also be partially stripped by the use of sodium bisulfite solutions or sulfurous acid, in the manner practiced in the bleaching of wool; but the stripping is only partial, and it is difficult to remove the sulfurous acid from the wool, and also the color is liable to return after a time.

Stannous chloride and hydrochloric acid will remove many of the acid colors; some of them, in fact, being stripped almost completely.

Another efficient stripping agent is potassium permanganate followed by a treatment with sodium bisulfite; almost any class of color may be removed to a greater or lesser extent by this method.

4. Stripping Basic Colors.

As these dyes are not much used on wool, this condition will seldom arise. Hot soap solutions will generally remove a considerable part of the color; and in the case of some colors, weak acid baths may be used to advantage. Treatment with chrome and sulfuric acid or with sodium hydrosulfite as outlined above is also a good means of removing basic colors. Stannous chloride and hydrochloric acid may also be employed for the removal of basic colors, and in many cases is a very good method.

5. Stripping Alizarine and Mordant Colors.

These are as a rule rather difficult to strip to any degree of satisfaction; but the use of chrome and acid will give good results in many cases. Sodium hydrosulfite will also decolorize many of these dyes. The natural dyes are more easily stripped than the alizarines; Log-

well in water and pass through a bath of dilute sulfuric acid till all trace of the chrome has been removed. Next treat with another bath for 6 hours at 100° F., and containing 100 gallons of water, 9 lbs. magnesium sulfate, and 3¼ lbs of sodium peroxide, the magnesium sulfate being added first in the preparation of the bath. Rinse well and pass into a third bath prepared in the same manner as the second, and leave for 8 hours at 100° F. Rinse well in water acidulated with sulfuric acid, then in a weak soap bath, then in water It is said that the shade obtained on rags by this method is quite light and the process does not injure the fiber.

[4] The principal compounds of this class that are used as stripping agents are Hyraldite Z, Rongalite, Decroline and Hydrosulfite NFX, Burmol and Formosul

Chapter XXVII.

Testing of Materials Used in Bleaching; Water.

1. Water.

A knowledge of the character of the water employed in the various operations of scouring and bleaching is something of considerable importance to the manufacturer. The qualitative analysis of water for purposes of scouring has already been gone over in a brief manner in a previous chapter, but the subject will now be taken up in more detail.[1]

2. Qualitative Tests.

The general qualitative analysis of water may be given as follows:

(*1*) *Free Acid.*—Place a sample of the water in a test-tube and add a few drops of a solution of lacmoid; if free acid is present the water will give a reddish color. To observe the color best the test-tube should be held over a white surface.

(*2*) *Free Alkali.*—A sample of the water in a test-tube is boiled for several minutes, then filtered and a few drops of phenolphthalein solution added. In the presence of free alkali the water will give a pink to reddish color.

(*3*) *Lime Salts.*—Take a sample of the water and boil until reduced to about one-tenth the original volume. Place some of this concentrated water in a test-tube and add a few drops each of solutions of ammonium oxalate and ammonium chloride. The presence of lime salts will be indicated by the formation of a white precipitate.

(*4*) *Magnesia Salts.*—Take the sample used in the preceding test and filter off from the lime precipitate. To the clear filtrate add a few drops each of ammonia and sodium phosphate solutions. A crystalline precipitate gradually forming will indicate the presence of magnesia.

(*5*) *Chlorides.*—To a sample of water which has been concentrated to one-tenth its volume add a few drops each of nitric acid and silver nitrate solution. The presence of chlorides will be indicated by the formation of a white precipitate.

(*6*) *Sulfates.*—To a sample of the concentrated water add a few drops each of hydrochloric acid and barium chloride solution. The presence of sulfates will be indicated by the formation of a white precipitate.

(*7*) *Bicarbonates or Free Carbonic Acid.*—To a sample of the original water add a clear solution of lime water. A cloudiness or white precipitate will indicate the presence of bicarbonates.

[1] The following statistical facts concerning water are interesting: The component parts of water by weight are oxygen 88.9, and hydrogen 11.1, and by volume, oxygen 1 and hydrogen 2. Water reaches its maximum density at 39.1° F., and at this temperature, 1 cubic inch weighs 252.6957 grains, 1 cubic foot weighs 62.425 pounds, and 1 c.c. weighs just 1 gram, or 1 liter weighs 1 kilogram. Water is 828.5 times heavier than air; its freezing point is at 32° F. (0° C.), boiling point at sea level is 212° F. (100° C.), while the temperature taken for the standard of specific gravities is 62° F. A cubic foot of ice weighs 57.25 pounds, and expands 0.089 = 1/11.24 of its bulk in freezing. One cubic foot of water contains 6.23 Imp. gallons, or 7.5 U. S. gallons; or 1728 cubic inches. One Imp. gallon of water contains 277.274 cubic inches or 10 lbs. One U. S. gallon of water contains 231 cubic inches or 8.3 lbs.

(8) *Iron.*—Take about 100 c.c. of the water and evaporate nearly to dryness, then add a few drops each of pure hydrochloric acid and nitric acid. Then add a few drops of a solution of potassium sulfocyanide when the formation of a red color will indicate the presence of iron. If a few drops of potassium ferrocyanide solution are added in place of the potassium sulfocyanide a blue color will be formed in the presence of iron.

For textile purposes, the principal characteristics to be determined in the analysis of a sample of water are *color, suspended matter, total solids, total hardness, temporary hardness, permanent hardness,* and *iron.*

3. Color.

For textile purposes, the color of a water, as a rule, has little influence on its utility, as under ordinary conditions this would not be sufficiently marked. In some waters that run through peaty districts a brownish or yellowish color is often apparent which may at times be sufficient to make the water undesirable for washing-off in final bleaching, but for scouring purposes it has but little influence. Color

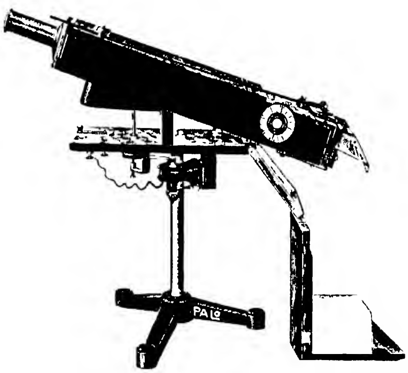

FIG. 296.—Hess-Ives Tint Photometer.

in water due to suspended matter is not to be considered as color of the water, for if a water has much color due to this cause, it would have sufficient suspended solid matter as to be unsuitable for use, and when the suspended matter is removed the color will also disappear. There is no standard of comparison for the color of water, and consequently it is difficult to give it a quantitative value. One of the best methods, perhaps, is to obtain the color value of a definite thickness of water in terms of a Lovibund or Hess-Ives tintometer, and give the total number of units of standard color glasses employed as the numerical value for the color of the water. To illustrate this method the following example is given:

Example.—A tube 10 ins. long was filled with distilled water and placed in one side of a Lovibund tintometer; its color was matched with the tintometer glasses in the other side of the instrument, giving 0.6 unit of color.

A sample of water for analysis was then substituted for the distilled water, and it required 8.25 color units in the tintometer. Hence, the quantitative color value of this sample of water referred to distilled water as unity, was $8.25 \div 0.6 = 13.7$.[2]

4. Suspended Matter.

River, or surface water in general, is liable to contain a considerable amount of suspended matter, though this amount may vary within large limits from time to time. Well water usually contains but a small amount, if any suspended matter. If the amount of suspended matter is quite appreciable, the water should be properly filtered or settled before use. The amount of suspended matter is readily determined by filtering one liter of the water through a tared filter, drying at 100° C. and reweighing.

Example.—A filter paper, dried in a weighing bottle in an air oven, weighed 0.685 gm. After filtering one liter of water to be tested through this paper, it was again dried in the weighing bottle at 100° C., and weighed 0.766 gm. Hence, the amount of suspended matter per liter in this water was 0.091 gm. or 91 parts per million.

5. Total Solids.

This includes both suspended matter and dissolved solids, and may be determined by boiling down one liter of the water in a large evaporating dish to a volume of about 50 c.c., then transferring this to a smaller porcelain or platinum crucible of known weight, and continuing the evaporation to complete dryness on a water bath and finally heating for a few minutes in an air oven at 110° C. The crucible is weighed again, and the increase in weight corresponds to the amount of solid matter per liter. By taking the difference between this amount and the figure for suspended matter, the amount of *dissolved solids* will be obtained.

Example.—One liter of water (same as taken for the preceding example) was placed in a porcelain dish and evaporated on a sand bath until only about 50 c.c. remained. This residue was transferred to a porcelain crucible weighing 25.762 gms. (A small amount of dried residue in the dish was washed into the crucible with a little distilled water.) The evaporation was continued to dryness on a water bath, and then the residue was heated in an air oven at 110° C. for 10 minutes. On cooling and reweighing, the result gave 25.977 gms. Hence, the total solids in this sample of water were 0.215 gm. per liter. As the suspended matter amounted to 0.091 gm., the amount of dissolved solids is 0.124 gm. per liter, or 124 parts per million.

[2] Olsen (*Quant. Anal.*, p. 382) gives the following method for the determination of color in water: The color is measured by a comparison with the color of a solution of platinum and cobalt salts, and is expressed in parts of platinum per million. A standard solution which has a color of 500 is made by dissolving 1.246 gms. of potassium platinic chloride ($PtCl_4.2KCl$), containing 0.5 gm. of platinum, and 1 gm. of crystallized cobaltous chloride ($CoCl_2.6H_2O$), containing 0.25 gm. of cobalt in water, with 100 cc. of concentrated hydrochloric acid, and making up to 1 liter with distilled water. By diluting this solution standards are prepared having colors of 0, 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, 70 parts per million. These are kept in 100 cc. Nessler jars of such diameter that the liquid has a depth of 20 to 25 cm. and is protected from dust. The color of a sample is observed by filling similar tube and comparing it with the standards. The observation is made by looking vertically downwards through the tubes upon a white surface placed at such an angle that the light is reflected upwards through the column of liquid. The reading is recorded to the nearest unit. Waters that have a color darker than 70 are diluted before making the comparison, in order that no difficulties may be encountered in matching the hues. Water containing matter in suspension is filtered until no visible turbidity remains.

6. Total Hardness.

This is really a measure of the soap-destroying power of a water, and is caused by the mineral matter present combining with the soap

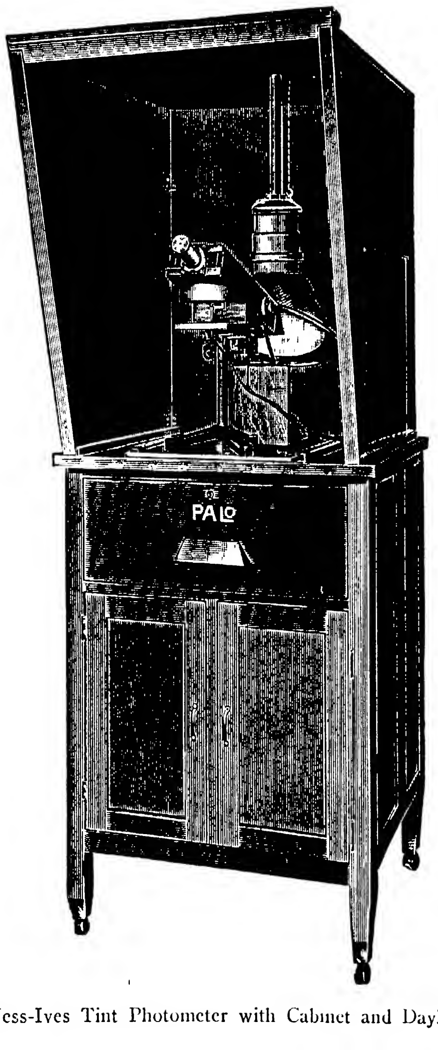

Fig. 297.—Hess-Ives Tint Photometer with Cabinet and Daylight Lamp.

to form an insoluble compound. It is to be expressed quantitatively in terms of milligrams of lime (CaO) per liter, which is equivalent to parts per million. Although all of the hardness may not be caused

by the presence of lime, as magnesium, aluminium, or other metallic salts may be present, yet for purposes of uniformity and convenience, the hardness is reckoned in this manner. A very convenient and practical method for determining the hardness of water is by the use of a standard soap solution. The method is carried out as follows: It is first necessary to prepare a standard hard water; this is done by dissolving 1.8 gms. of pure calcium carbonate in the least quantity of hydrochloric acid, evaporating to dryness to expel any excess of acid, and then dissolving the residual calcium chloride in water and diluting the solution to 1000 c.c. This solution will represent 1 gm. of lime (CaO) per liter. The soap solution is prepared by dissolving 20 gms. of pure soap in 500 c.c. alcohol and diluting to 1 liter with water.[3] This soap solution is then standardized by placing 10 c.c. of the standard hard water in a small flask together with 90 c.c. of distilled water. The soap solution is placed in a burette, and gradually added to the hard water. After each addition of the soap solution the flask is well shaken and when a permanent lather (one lasting 5 minutes) is obtained, the amount of soap solution added is noted.[4] This titration is then repeated in the same manner with 100 c.c. of distilled water in place of the hard water, and the amount of soap solution required to produce a permanent lather is again noted. The latter number is subtracted from the former,[5] and the remainder indicates the amount of soap solution necessary to neutralize 0.010 gm. This latter figure divided by the number of c.c. of soap solution used will give the quantity of lime which one c.c. of the soap solution will neutralize. Having thus standardized the soap solution, the hardness of any sample of water may be determined by titrating 100 c.c. with the soap solution as above described.[6]

Example.—The soap solution prepared as above required 11.6 c.c. to neutralize 10 c.c. of the standard hard water and 2.2 c.c. to neutralize 100 c.c. distilled water. Hence, 9.4 c.c. of the soap solution were equivalent to 0.010 gm. of lime, or 1 c.c. was equivalent to 0.00106 gm. of lime. A sample of water for analysis required 6.6 c.c. of the soap solution to neutralize 100 c.c.; hence,

[3] Nelson (*Chem. News*, Sept. 13, 1889) gives the following method for the preparation of a standard soap solution: 1 gm. of pure palmitic acid is dissolved in a small volume of pure alcohol, and neutralized with 4 c.c. of normal caustic soda solution. This volume of soda solution is equivalent to 4 x 50 mgms. calcium carbonate, therefore it is diluted to 200 c.c., adding sufficient alcohol so that its percentage in the standard solution amounts to 35.

[4] Buchner (*Chem. Zeit.*, Dec., 1892) points out the fact that it is important, in order to obtain constant results, to keep the solutions during the titration at about 15° C., for a lather which will remain for 5 minutes at this temperature will disappear in less than 1 minute at a temperature of 25° C. In the determination of hardness of water in summer this point should be borne in mind.

[5] It is perhaps more accurate, instead of subtracting this figure for distilled water from that of the standard hard water, to make note of it and subtract each time a hard water is tested; in which case the standardization of the soap solution would be effected by simply dividing the number of c.c. of soap solution used in the titration into 0.010 gm., which would give the value in terms of lime of each c.c. of the soap solution. For a soap solution which is practically equivalent in strength to the above lime solution, it is the custom to allow 1 c.c. of the former as a correction for neutralizing 100 c.c. of distilled water.

[6] The soap test method of determining the hardness of water is not adapted for use in the presence of much magnesia; although as a measure of the soap-destroying power of the water it is always suitable. When the hardness of water is desired for other purposes than with reference to the soap-destroying power, this method can only give approximate results, and in some cases, even, the results may be quite misleading.

its hardness was 0.067 gm. per liter, or 67 parts per million. This method of determining the hardness may have many theoretical flaws, but it affords a quick and practical test which represents the soap-destroying power of the water with considerable accuracy.[7]

The manner of representing the degrees of hardness of water varies somewhat in different countries, as follows:

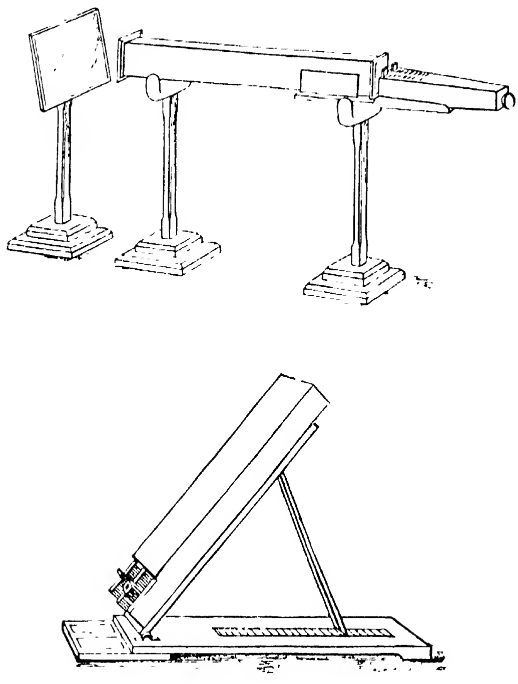

FIG. 298.—Lovibund Tintometer.

English scale, $1° = 1$ grain calcium carbonate ($CaCO_3$) per gallon of water[8] = 1 part in 70,000.

German scale, $1° = 1$ part lime (CaO) per 100,000 parts of water.

French scale, $1° = 1$ part of calcium carbonate ($CaCO_3$) per 100,000 parts of water.

The relation between these various scales is shown as follows:

[7] When a water is so hard as to require a greater amount of soap solution for 100 c.c. of the water than suffices to neutralize 23 mgm. of lime, better results are obtained by diluting the water with an equal bulk (or more if necessary) of pure water, inasmuch as too heavy a precipitate of calcium soap appears to interfere with the proper lathering. Of course, the influence of the additional quantity of water must be allowed for (Mason, *Examination of Water*).

[8] This is known as the "Clark scale," and is still in use in England; each degree corresponds to one grain of calcium carbonate per imperial gallon of water, or one part in seventy thousand. Water is considered soft when below 6 degrees of hardness.

English	German	French	English	German	French
0.62	0.50	0.90	6.25	5.	8.95
0.70	0.56	1.00	7.50	6.	10.74
1.00	0.80	1.43	8.75	7.	12.55
1.25	1.00	1.79	10.00	8.	14.30
2.50	2.00	3.58	11.25	9.	16.08
3.75	3.00	5.37	12.50	10.	17.90
5.00	4.00	7.17			

By multiplying the degrees in the German scale by 10 the degrees in milligrams of calcium carbonate per liter or parts per million will be obtained.[9]

The more modern method (at least in America) of expressing hardness is in milligrams per liter, corresponding to parts per million.

A modification of the soap method of determining the hardness, is given as follows: 0.523 gm. of pure crystallized barium chloride ($BaCl_2.2H_2O$) is dissolved in water, and the solution made up to 1000 c.c. The quantity of barium chloride contained in 100 c.c. of this solution corresponds to 12° (Ger.) of hardness. The soap solution is prepared as above described. Then 100 c.c. of the barium chloride solution are placed in a flask and titrated with the soap solution, and the latter is suitably diluted with alcohol (56 percent) so that 45 c.c. exactly correspond with 100 c.c. of the barium chloride solution. Next, 100 c.c. of the water to be tested is titrated with the corrected soap solution, and the hardness of the water (which is not proportional to the amount of soap solution used) is obtained by reference to the following table:

TABLE I

Soap solution c.c.	Hardness degrees (German)	Soap solution c.c.	Hardness degrees (German)	Soap solution c.c.	Hardness degrees (German).
3.4	0.5	18.9	4.5	34.7	8.9
4.2	0.7	19.7	4.7	35.3	9.1
5.0	0.9	20.4	4.9	36.0	9.3
5.8	1.1	21.2	5.1	36.7	9.5
6.6	1.3	21.9	5.3	37.4	9.7
7.4	1.5	22.6	5.5	38.1	9.9
8.2	1.7	23.3	5.7	38.4	10.0
9.0	1.9	24.0	5.9	38.7	10.1
9.8	2.1	24.8	6.1	39.4	10.3
10.5	2.3	25.5	6.3	40.1	10.5
11.3	2.5	26.2	6.5	40.8	10.7
12.1	2.7	26.9	6.7	41.5	10.9
12.8	2.9	27.6	6.9	42.1	11.1
13.6	3.1	28.4	7.1	42.4	11.2
14.3	3.3	29.1	7.3	42.8	11.3
15.1	3.5	29.8	7.5	43.1	11.4
15.9	3.7	30.5	7.7	43.4	11.5
16.6	3.9	31.2	7.9	43.7	11.6
17.4	4.1	31.9	8.1	44.0	11.7
17.8	4.2	32.6	8.3	44.4	11.8
18.1	4.3	33.3	8.5	44.7	11.9
18.5	4.4	34.0	8.7	45.0	12.0

[9] Water is said to be *hard* when it contains more than 10 parts of mineral matter per 100,000; or more than 7 grains per gallon, or 100 parts per million (p. p. m.). A water of satisfactory softness for bleaching should contain less than 50 p. p. m. of hardness.

TABLE II

Soap solution c.c.	Degrees of Hardness	Difference	Soap solution c.c.	Degrees of Hardness	Difference
1.4	0°	....	24	5.87	0.28
2	0.15	0.25	25	6.15	0.28
3	0.40	0.25	26	6.43	0.28
4	0.65	0.25	27	6.71	0.28
5	0.90	0.25	28	6.99	0.28
6	1.15	0.25	29	7.27	0.28
7	1.40	0.25	30	7.55	0.28
8	1.65	0.25	31	7.85	0.29
9	1.90	0.26	32	8.12	0.29
10	2.16	0.26	33	8.41	0.29
11	2.42	0.26	34	8.70	0.29
12	2.68	0.26	35	8.99	0.29
13	2.94	0.26	36	9.28	0.29
14	3.20	0.26	37	9.57	0.30
15	3.46	0.26	38	9.87	0.30
16	3.72	0.26	39	10.17	0.30
17	3.98	0.27	40	10.47	0.30
18	4.25	0.27	41	10.77	0.30
19	4.52	0.27	42	11.07	0.31
20	4.79	0.27	43	11.38	0.31
21	5.06	0.27	44	11.69	0.31
22	5.33	0.27	45	12.00	....
23	5.60	0.27			

Another method of conducting the test for hardness is to prepare a standard hard water by using just 1 gm. of calcium carbonate, dissolving in hydrochloric acid, evaporating to dryness, and diluting to 1 liter as before described. The soap solution is then so prepared that 1 c.c. will neutralize just 1 milligram of calcium carbonate. To determine the hardness in parts of calcium carbonate per 100,000 it is then necessary to use 100 c.c. of the water for analysis; if the result is to be in grains per English gallon, 70 c.c. of the water are taken and if in grains per U. S. gallon 58.3 c.c. are taken. In some cases, when using a soap solution so that 1 c.c. corresponds to 1 milligram of calcium carbonate, it is customary to deduct 1 c.c. from the reading for correction due to amount of soap solution required to produce a lather with distilled water, and using the remainder for calculating the degrees of hardness.[10]

7. Temporary and Permanent Hardness.

The permanent hardness of water, due to dissolved sulfates or chlorides of the metals, is determined in the same manner as above described, only the sample of water being tested is boiled before its hard-

[10] Gasslin recommends the following method for the determination of total lime in water: 50 c.c. of a centinormal solution of oxalic acid and two drops of ammonia are added to 50 c.c. of the water under examination. The mixture is well shaken, and after 10 minutes, is filtered, and the amount of oxalic acid remaining in the filtrate is estimated by titration with a centinormal solution of potassium permanganate. The difference between this latter number and the 50 c.c. of oxalic acid originally added gives the number of c.c. of centinormal oxalic acid neutralized by the lime in the water. Each c.c. of centinormal oxalic acid solution is equivalent to 0.00028 gm. of lime, CaO.

ness is determined. In the operation of boiling the temporary hardness, due to dissolved bicarbonates of the metals, is destroyed, leaving only the permanent hardness remaining; so that by taking the difference between the total and the permanent hardness the temporary hardness is obtained. The test is carried out as follows: 100 c.c. of the water to be examined are boiled vigorously for ten minutes, then allowed to cool, and the volume made up again to 100 c.c. by the addition of distilled water; it is then titrated with the soap solution as previously described.

Example.—A sample of the water employed for analysis in the previous example, on treatment as above described, required 5.1 c.c. of soap solution to neutralize the hardness in 100 c c. after boiling. As each c.c. of the soap solution is equivalent to 0.00106 gm. of lime, the permanent hardness in this case would be 54 parts per million, and as the total hardness was 67, the temporary hardness would be 13 parts per million.

Another method for the determination of hardness in water is by titration with standard acid (Hehner's method). The method is conducted as follows: 100 c.c. of the water to be analyzed are placed in a flask, a few drops of Methyl Orange are added, and then 1/50-normal sulfuric acid is added from a burette until the color of the water changes from a yellow to a reddish tint. Each c.c. of acid required corresponds to 0.001 gm. of calcium carbonate or to 0.00056 gm. of lime. This measures the temporary hardness.[11] To determine the permanent hardness, to 100 c.c. of the water there are added 50 c.c. of a 1/50-normal sodium carbonate solution, and the mixture is boiled for about 30 minutes (if magnesium salts are present, it will be necessary to evaporate to dryness and take up the residue with water). Filter, and make up the filtrate to 100 c.c. Titrate this with 1/50-normal acid as before using Methyl Orange as an indicator. The acid is used up in neutralizing the excess of sodium carbonate beyond that needed to precipitate the sulfates or chlorides of the metals; as each c.c. of acid is equivalent to one c.c. of sodium carbonate, by taking the difference between the original 50 c.c. of sodium carbonate solution added and the number of c.c. of acid used, we will have the number of c.c. of sodium carbonate required to precipitate the metallic salts in the water. Each c.c. of sodium carbonate thus used will correspond to 0.001 gm. of calcium carbonate or 0.00056 gm. of lime.[12]

[11] In using Hehner's method for determining the temporary hardness of water by titration with 1/50 normal acid and with Methyl Orange as an indicator, it must be borne in mind that a certain small quantity of acid is required to effect the change of color in the indicator, and when such dilute solutions are being operated on, this may bring quite a large error into the results. The necessary correction to use may be discovered by titrating a sample of distilled water to which the same number of drops of Methyl Orange are added as are employed in the water being tested, and noting the quantity of acid required to give a reddish color The sample of hard water should be titrated until its color just matches that in the distilled water, and the amount of acid required for the latter is deducted as a correction from the volume of acid used in the titration of the hard water.

[12] According to Teed (*Jour. Soc. Chem. Ind.*, 1889, p. 256), each equivalent of lime in hard water destroys one and one-third molecular equivalents of soap (as sodium oleate), while one equivalent of magnesia destroys one and one half equivalents of soap. On this basis, one molecule of calcium sulfate will neutralize two and two-thirds molecules of soap, or one molecule of magnesium sulfate will neutralize three molecules of soap. Due to this fact the soap method for determining the hardness of water gives a more practical result for the use of water in scouring and bleaching, than the determination of the hardness by titration with acid. According to Richardson (*Jour. Soc. Dyers & Col.*, 1893, p. 194) one molecule of calcium as chloride will destroy 2.8 molecules of soap as oleate, and one

Example.—100 c.c. of a sample of water on titration with $^1/_{50}$-normal sulfuric acid, required 6 c.c. of acid for neutralization, which is equivalent to 34 parts of lime per million as temporary hardness; 100 c.c. of the water boiled with 50 c.c. of $^1/_{50}$-normal sodium carbonate solution and filtered, on titration with $^1/_{50}$-normal sulfuric acid, required 46.7 c.c. for neutralization; hence, 3.3 c.c. of $^1/_{50}$-normal sodium carbonate were used up in precipitating the metallic salts, which corresponds to 18.4 parts of lime per million as permanent hardness. The total hardness of this water would consequently be 52.4 p. p. m. of lime.

Instead of using Methyl Orange as the indicator, it is said that more accurate results are obtained employing a drop of a mixture of 1 gm. of pure alizarine paste in 200 c.c. of water. The change in color of this indicator is from violet in alkaline solution to yellow in neutral or acid solution. Unfortunately the indicator is affected by carbonic acid, and consequently, the titration must be finished at the boil. The titration is carried out with 1/10-normal hydrochloric acid in a porcelain basin, the acid being added in the cold until the color of the indicator changes to yellow, when the liquid is boiled and the violet color will return owing to the escape of carbonic acid gas; another drop of acid is added, and so on until no further change takes place.

In the preceding methods for determining the hardness of water no distinction is drawn between that caused by lime salts and that due to salts of magnesia. In order to be able to prescribe satisfactorily just what additions should be made to the water for the correction of the hardness, it is sometimes desirable to know the proportion of hardness due to magnesia. The *amount of magnesia* in a hard water may be determined as follows: 100 c.c. of the water are neutralized with 1/10-normal hydrochloric acid in the presence of alizarine indicator in boiling solution. 25 c.c. of clear lime-water are measured into a 200 c.c. flask and the hot neutralized hard water is also added, and the whole made up to somewhat over the mark (to allow for contraction in cooling) with hot distilled water. The flask is stoppered and well shaken, and then set aside to cool and settle. When the liquid is completely clear, pipette off 100 c.c. and titrate back with 1/10-normal acid with phenolphthalein indicator. Then titrate an equivalent amount of lime-water (12.5 c.c.). Deduct the amount of acid required for the mixture of lime-water and the hard water from that employed for the lime-water alone, and multiply the difference by 5, which will give the hardness due to magnesia in terms of calcium carbonate per 100,000. From this, the actual magnesia may be calculated by multiplying by

molecule of magnesium as sulfate would require 4.2 molecules of soap These figures are considerably higher than those of Teed given above; but Richardson has also found that these ratios change with the ratio of the saline constituents present in the water, and the degree of dilution and temperature, the greater the proportion of magnesium sulfate to the soap, with the same volume of water, the fewer is the number of soap molecules decomposed. Allen (*Jour. Soc. Chem. Ind.*, 1888, p 797) has also found that a water containing both lime and magnesia does not destroy as much soap as the same amounts of lime and magnesia would do separately. Another point of interest in this same connection is that in the determination of temporary hardness it is presumed that calcium carbonate is totally insoluble in water free from carbonic acid gas; but this is not quite true, for Fresenius has given the solubility of calcium carbonate in water as about 2.5 grains per gallon Hence in determining the temporary hardness in terms of calcium carbonate, about 2.5 degrees (if figured in grains per gallon) should be added to the result as generally found. From this it may be seen that 2.5 grains per gallon of lime hardness may be due to carbonate, and in the same manner about 6 grains per gallon of magnesium permanent hardness may be due to carbonate, this being the amount of magnesium carbonate soluble.

the factor 0.24 for Mg, or by 0.4 for MgO. The principle of the method is that the lime-water precipitates the magnesia salts, but has no effect on the lime salts.

In order to calculate out the quantities of lime and soda ash necessary to add to a hard water (expressed in German degrees of hardness) for purposes of softening, the following formulas may be used:

Let T = temporary hardness
P = permanent hardness
M = hardness due to magnesia
Then, 5.6 x (T + M) = amount of lime (CaO) required;
10.6 x P = amount of soda ash required,
or, 28.6 x P = amount of soda crystals required.

If only the temporary hardness is to be corrected by the addition of lime, the quantity required is:

$$5.6 \times (T + H - P)$$

if M is larger than P, but if not, only the temporary hardness need be taken into account.

For softening with caustic soda and soda ash, we have:

8 x (T + M) = amount of caustic soda required.
10.6 x — (T + M) = amount of soda ash required.

In waters containing *free dissolved carbon dioxide* gas (in addition to that present as temporary hardness), the amount may be determined as follows:[13] 100 c.c. of the water are slowly titrated with 1/10-normal sodium carbonate solution with phenolphthalein until a permanent pink color is obtained. The number of c.c. used multiplied by the factor 2.2 gives the parts of carbon dioxide, CO_2, per 100,000; or multiplying by the factor 2.8 will give the amount of lime, CaO, required to remove it.

McGill gives the following formulas for use in water analysis, based on milligrams per liter or parts per million:

Let v = c.c. of $^1/_{10}$-normal hydrochloric acid used in titrating 100 c.c. of the sample with phenolphthalein as indicator;

w = c.c. of $^1/_{10}$-normal hydrochloric acid used in finishing the above titration with Methyl Orange as indicator;

H = total hardness, obtained as follows: after finishing the titration of 100 c.c. of the water with $^1/_{10}$-normal hydrochloric acid and Methyl Orange, 25 c.c. of a $^1/_{10}$-normal "soda-reagent" (in which one-half the soda is present as carbonate and one-half as hydrate) are added and the liquid boiled; it is then cooled and made up to 200 c.c., filtered, and 100 c.c. of the filtrate are titrated back with $^1/_{10}$-normal hydrochloric acid. Let Q^1 = c.c. of the "soda-reagent" used, and r^1 = c.c. of $^1/_{10}$-normal hydrochloric acid used in the back titration;

Hp = permanent hardness, obtained by titrating 100 c.c. of the sample till neutral to phenolphthalein, then adding 25 c.c. of the "soda-reagent," boiling a few minutes. Then cool, make up to 200 c.c., filter, draw out 100 c.c. and titrate back with $^1/_{10}$-normal hydrochloric acid. Let Q^2 = c.c. of the "soda-reagent" used, and r^2 = c.c. of hydrochloric acid used in back titration; then the following formulas may be deduced:

[13] For the determination of free carbonic acid in a water, Vignon recommends a titration with a standard solution of calcium hydrate, using phenolphthalein as the indicator. It is claimed that by this method the carbonic acid may be estimated rapidly and with great accuracy.

Carbon dioxide (CO_2) in monocarbonate $= 22v$.
Carbon dioxide (CO_2) in bicarbonate $= 44w$.
Total combined carbon dioxide $= 22(v+2w)$.
"Alkalinity" $= A = 28\ (w+v)$.
Total hardness $= H = 28\ (Q^1 - 2r^1)$.
Permanent hardness $= Hp = 28\ (Q^2 - 2r^2)$.
True temporary hardness $= Ht = H - Hp$.

Where "alkalinity" exceeds the true temporary hardness, it is due to presence of sodium carbonate,

$$\text{Sodium carbonate (naturally present)} = \frac{53}{28}(A - Ht).$$

"Causticity," or alkalinity to phenolphthalein, $a = 28v$.

To determine the amount of lime (CaO), take 250 c.c. of the sample, add an excess of ammonium oxalate solution, filter off the precipitated calcium oxalate, wash with hot water, dissolve from filter in sulfuric acid, heat, and titrate with $^1/_{10}$-normal potassium permanganate solution. Let k = c.c. of potassium permanganate used, then

Lime, (CaO) $= 11.2k$.

8. Iron.

As the presence of iron in water is especially deleterious when the water is to be employed for purposes of dyeing and bleaching, it is desirable to have an accurate and rapid method for the determination of small quantities of iron in water. As a rule the amount of iron actually present in any sample of water is relatively very small, and in most cases a quantitative analysis is not necessary. To determine the presence of iron in water, take about 100 c.c. of the sample and evaporate it down in a porcelain dish to about 10 c.c.; then add a few drops of a solution of potassium sulfocyanide to a portion of this residue. If the water remains clear, no iron is present, but if a reddish color is produced, then iron is indicated. To the remaining portion of the water, add a few drops of a solution of potassium ferrocyanide, and if a bluish color is produced the presence of iron is also indicated. In carrying out these tests care should be exercised that no trace of iron gets into the water while it is being evaporated down; it is well to cover the evaporating dish with a large watch glass. This test may be made quantitative, by starting with just 100 c.c. of the water, evaporating to about 10 c.c., adding a definite number of drops of potassium sulfocyanide solution, and putting the water in a long test-tube held against a white background. By using other similar test tubes containing definite amounts of ferric chloride in solution, and to which have been added the same number of drops of potassium sulfocyanide solution as to the sample, a comparison may be obtained until an iron solution giving the same depth of color as the sample is reached, when the actual amount in the sample may then be known.[14]

9. Interpretation of Water Analyses.

As to the interpretation to be placed upon the results of the analysis of any sample of water, it may be said that if the hardness is below 50 parts per million, the water may be considered soft, whereas, if it

[14] Lunge and Keller, *Zeit. ang. Chem.*, 1896, p. 3, and Seyda, *Chem. Zeitung*, 1896, p. 1086.

reaches to 150 parts the sample must be regarded as quite hard. The following table represents the average hardness (in terms of calcium carbonate) of a large number of samples of the waters specified:

	P. p. m.
Rain water	3
Upland surface water	54
Deep well water	250
Spring water	185

It will be seen from this that river water, as a rule, is much softer than spring or well waters, even though it may contain a much greater amount of suspended solids.[15] This is due to the fact, of course, that river water is mostly derived from the surface of the earth, and not having percolated through the ground, as would be the case with well or spring water, it has dissolved less mineral matter. On the other hand, well and spring waters are usually much clearer than river water, hence it may be readily understood that the appearance of a water is no criterion as to its degree of hardness, which can only be determined by actual analysis.

[15] Leed's standard of hardness for American rivers is 50 for soft and 150 for hard, expressed in p. p. m.

Chapter XXVIII.

Testing of Materials Used in Bleaching; Alkalies.

1. Alkalies.

As alkalies are very largely employed as detergents for wool, careful consideration should be given to the character of these bodies entering into the composition of the scouring bath, for it has already been pointed out that the chief cause for the deterioration of the wool fiber, which may be brought about by the process of scouring, lies in the improper use of the alkali. For this reason, the nature and properties of the various alkalies employed in scouring should be thoroughly understood if it is desired that the operation should be intelligently conducted.

In its chemical sense an "alkali" means a strong base, and for all practical purposes the alkalies in common use may be taken as the hydroxides of potassium, sodium and ammonium, together with the carbonates of these same elements; in addition to these, calcium hydroxide, or quicklime, is also considered as an alkali. In their general action alkalies are corrosive, and especially is this true of the alkaline hydroxides, from which fact these latter are usually distinguished as the "caustic" alkalies. For instance, the hydroxides of potassium and sodium are known respectively as caustic potash and caustic soda, and calcium hydroxide is known as caustic lime. The alkaline carbonates are much milder in their general chemical action than the corresponding hydroxides, and are usually spoken of as "soda" and "potash," meaning sodium carbonate and potassium carbonate respectively. Both ammonium hydroxide and carbonate are volatile, hence these bodies are known as the "volatile" alkalies in contradistinction to the compounds of sodium and potassium, which are known as the "fixed" alkalies.

As already mentioned, *lant* (stale urine) was once largely employed for the purpose of scouring wool, and excellent results are said to have been obtained by its use, the cleansing being thorough and the good qualities of the fiber being left unimpaired. The detergent qualities of lant are due to the ammonium carbonate which it contains in considerable amount. This ammonium carbonate is produced in the decomposition of the nitrogenous matter originally present in the urine, such decomposition probably taking place through the agency of fermentation. If it were not for the disagreeable features of lant, it might still be employed effectively for the scouring of wool, but it is liable to cause a discoloration of the fiber and also leaves the material with an unpleasant odor which is difficult to completely eliminate.

Many scouring compounds on the market contain a small quantity of ammonium sulfate in admixture with soda ash, so that when the compound is dissolved in water it will evolve a copious odor of ammonia and lead the user to imagine the preparation in question contains a large amount of ammonium carbonate. In order to prevent the gradual decomposition of the ammonium salt by the soda ash before being used, the particles are covered with a protecting medium consisting of a paraffin oil, size, or wax, and the preparation so made is incorporated with the soap powder or other material used. Under the best conditions, however, these preparations gradually lose their ammoniacal constituent.

Sodium silicate (soluble glass), *borax*, and other alkaline salts are at times employed for scouring, or at least in conjunction with other scouring agents. They are rather mild in their scouring action, and at times the exact reason for their use is not very apparent. Soluble glass is frequently added to soap as a filling or weighting material, giving a product which may contain a very high percentage of water, and yet appear hard and dry. Its use in this connection is not a legitimate one and such soaps should be rejected as impure.[1]

The addition of certain mineral oils to the soap or other scouring liquors has been suggested, and under certain conditions their use may be productive of good results, due, no doubt, to their great solvent action on the wool fat. Unless their use is carefully understood, however, it will be found difficult to remove such oils from the fiber completely, and subsequent stains may be the result. Due to the fact, however, that most of these oils are more or less volatile, the last traces of them may usually be removed by careful drying, though this procedure is not always convenient where the material is to be dyed immediately after scouring.

In former times the bark of a tree known as *quillaia* was used quite extensively as a detergent in wool scouring. It derives its name from the Chilian word *"quilloan,"* meaning to wash, and is obtained from a tree belonging to the *Rosaceæ*, growing in several South American countries. The principal species of which use is made is the *R. saponaria*, a white flowering tree growing to a height of 50 or 60 feet. The infusion of the bark is also used as a hair tonic. The useful ingredients of the bark, as far as scouring is considered, are two in number. The principal one is *saponine*, $C_{32}H_{54}O_{18}$, is also known as *senegin*, a glucoside of *sapogenine*. Saponine may be obtained from the bark by extraction with boiling alcohol. It has great lathering and cleansing power, and also readily emulsifies oils; in this latter effect it is assisted by *pectin*, the second constituent of the quillaia bark. The

[1] Sodium silicate (soluble glass) has apparently some advocates among wool scourers; it is said to be much cheaper than soap, and possesses the property of readily emulsifying fatty matters without injuring the wool fiber. When employed for wool scouring, however, the sodium silicate should be free from caustic soda, the solution should be dilute, and the temperature should not be very elevated. According to the *conceria italiana*, the following method is employed in practice: 2.5 kilos. of sodium silicate is dissolved in 100 liters of water and heated to 50° C. The wool is scoured in this bath for 10 to 12 minutes, then washed for 20 minutes in a second bath heated to 35 to 40° C. and containing 1 part of sodium silicate to each 100 parts of wool. The wool is finally washed well in cold water It is said that the cost of scouring with sodium silicate is only 40 percent of that when soap is used, but this is to be strongly doubted.

detergent action of quillaia, however, is distinctly inferior to soap. For washing purposes the clear solution obtained by macerating the crushed bark in cold soft water is used.

The following process is given for the use of quillaia bark or saponine extract in scouring: 150 grams of finely chipped bark are boiled with 600 liters of water containing 5 to 7 kilos. of formaldehyde solution and sufficient sulfuric acid to give an acid reaction. The liquor filtered from the bark is then boiled in a steam-jacketed vessel to the consistency of a syrup, after which it is allowed to stand for about 12 hours to allow the calcium sulfate present to settle. The latter is removed, and the extract may then be evaporated to dryness with constant stirring. The dry mass so obtained is pulverized, and the saponine so produced is of a yellowish gray color, and dissolves in water to a clear solution of a soapy feel and consistency.[2]

Infusions of other plants such as the marsh-mallow, comfrey and quince, also possess saponaceous qualities, but not to the same extent as quillaia bark.

Infusions of other plants, such as the marsh-mallow, comfrey and is not precipitated either by alcohol or by ether. The infusions of other plants which might be substituted for quillaia differ from it in as much as they do not reduce Fehling's solution, so that this test may be taken as a means of guarding against fraudulent substitution. Genuine quillaia bark is also very heavy and will sink in water. A determination of the amount of ash contained in a sample will also show at once any adulteration, as genuine quillaia bark gives about 14 percent of ash. Another characteristic appearance of quillaia bark is the occurrence of crystals of calcium carbonate (arragonite) when thin sections of the sample are viewed under the microscope.

2. Sodium Carbonate.

This is probably the alkali most largely employed in the scouring of wool. It acts as a very efficient emulsifying agent and is also quite cheap in comparison with soaps and potash salts. It is commonly known by the name of *soda*, a term which was originally used in the Middle Ages to designate an alkali, and included the alkaline salts derived from both wood-ashes and the ashes of sea plants. In early times a distinction was drawn between the alkali of potash and that of soda, owing to the erroneous opinion that potash was entirely of vegetable origin, while soda was to be found only in the mineral kingdom. On this account potash was known as *vegetable alkali* and soda was known as the *mineral alkali*. Both of these alkalies were at first regarded as elementary substances, and, in fact, it was not until 1807 that Davy proved that they were compounds of two metals, potassium and sodium respectively.

The chemical formula for sodium carbonate is Na_2CO_3. It is brought into trade in a variety of forms and under a number of names. The product known as *soda ash*, or simply as *soda*, is a white (occasionally slightly yellowish) amorphous powder, and is obtainable in a

[2] R. Stahmer, *Ger. Pat*, 116,591 of 1900.

high degree of purity, containing from 96 to 98 percent of pure sodium carbonate. Another product known as *sal soda, crystal soda* or *washing soda* is the ordinary form of soda employed for domestic purposes; it differs from soda ash in being crystalline and containing a large quantity of water of crystallization, its composition corresponding to the formula $Na_2CO_3.10H_2O$, and containing about 63 percent of water and 37 percent of soda ash. In practical value, about 100 parts by weight of crystal soda are equal to about 37 parts of soda ash; or to obtain the equivalent of 100 parts of the latter it is necessary to take 270 parts of crystal soda. In former times sal soda was greatly in demand, for being crystalline in structure, it was usually much purer in quality than soda ash, the latter being especially liable to contamination with salts of iron and aluminum, two very objectionable impurities when the alkali was to be employed in connection with soap. Sal soda is very efflorescent in dry air; that is to say, it readily parts with its water of crystallization, loses its crystalline structure, and crumbles to a fine white powder, the composition of which is $Na_2CO_3.H_2O$. Therefore, it is erroneous to presume that the powdered and dried sal soda is exactly the same in composition as ordinary soda ash, for it still contains one molecule of water which can only be completely eliminated by heating to rather a high temperature. Crystal soda is more readily soluble in water than is soda ash, the latter being apt to form hard lumps which are difficult to dissolve; 100 parts of water will dissolve 7 parts of soda ash cold and 45 parts at the boil; the same quantity of water will dissolve 21 parts of crystal soda cold or 420 parts at the boil. There is, however, a peculiarity in the solubility of sodium carbonate in water in that the maximum solubility is not at the boiling temperature, but at about 90° F., for while the solubility at the boil is 45 parts, the solubility at 90° F. is 59 parts per 100 of water.

Crystal carbonate is another form of sodium carbonate; it occurs as small crystals of a high degree of purity, and contains much less water of crystallization than sal soda. Its composition appears to correspond to the formula $Na_2CO_3H_2O$, and it therefore contains between 14 and 15 percent of water.[3]

Sodium bicarbonate differs somewhat in its chemical nature from soda ash in that it is a salt in which the acid radical (carbonic acid, H_2CO_3) is not completely saturated with the base (soda, Na_2O), its formula being $NaHCO_3$, hence its name of *sodium hydrogen carbonate*. From the fact that the acid is not completely saturated in this salt, it might at first be supposed that the compound would exhibit acid characteristics; but, on the contrary, it is quite a strong alkali. This circumstance is accounted for by the fact that carbonic acid is a very

[3] The following analyses show the comparative composition of crystal carbonate and soda crystals.

	Crystal Carbonate	Soda Crystals
Sodium carbonate	82.90	34.22
Sodium hydrate	...	0.10
Sodium sulfate	trace	2.54
Sodium chloride	trace	0.27
Water	17.00	62.84

weak acid, whereas soda is a very strong base, so that with the acid portion only half saturated, the salt is strongly alkaline owing to the preponderating alkaline character of the base; this also explains the reason why soda ash itself is a strong alkali rather than a neutral salt. Sodium bicarbonate, however, is considerably milder in its alkaline character than soda ash; on which account it is sometimes recommended as a substitute for the latter in scouring where it is not desirable to employ too strong an alkali. Sodium bicarbonate is more soluble in water than soda ash; the following table gives the solubility in 100 parts of water at different temperatures of the two compounds:

	50°F.	68°F.	86°F.	104°F.	
Sodium bicarbonate,	12 6	21.4	38 1	50	parts.
Soda ash,	8.8	9 8	10 8	11.7	"

When sodium bicarbonate is heated (calcined) it loses a molecule of carbonic acid and is converted into soda ash. Even when a solution of sodium bicarbonate is heated, a portion of the carbonic acid is given off, and the solution on cooling will deposit crystals consisting of a mixture of the normal carbonate and the bicarbonate, corresponding to the formula $Na_2CO_3.2NaHCO_3.2H_2O$, which is known as *sodium sesquicarbonate*. When the solution of sodium bicarbonate is boiled for a considerable length of time, the conversion into the normal carbonate is complete. Natural deposits of sodium sesquicarbonate are to be found in certain districts of Egypt, Africa, and South America, and a few other localities. The mineral of which these natural deposits are formed is known as *Trona*, a term from which the word *natrium* is derived; the latter being the Latin name for sodium, from which is derived the symbol "Na" used to designate this element.

Soda ash when exposed to dry air is stable, but it will absorb a considerable amount of moisture in contact with damp air, though it in no case loses its solidity. In this respect it differs considerably from potash, which rapidly takes up moisture even from air of ordinary dryness, and soon becomes pasty in consistency. In its chemical properties, soda ash has a caustic taste and a strongly alkaline reaction; it melts at about 1465° F., and is not volatile. Soda ash and its solutions are decomposed by nearly all acids (even comparatively weak ones) with the liberation of carbon dioxide gas.

The solubility of sodium carbonate in 100 parts of water at different temperatures is given in the following table:

Temperature.	Parts of soda ash dissolved.
32°F.	7.1
42°F.	9.5
50°F.	12.6
59°F.	16 5
68°F.	21 4
86°F.	38.1
90°F.	59.0
94°F	46.2
174°F.	46.2
212°F.	45.1

Soda is usually designated in trade as LeBlanc or Solvay soda, depending on the method of manufacture. The latter is also sometimes called *ammonia soda.* LeBlanc soda is made by treating common salt, NaCl, with sulfuric acid, and subsequently heating the salt cake so obtained (consisting principally of sodium sulfate) with coal and limestone, which causes the formation of sodium carbonate. The product obtained in this manner is very impure, containing in admixture various other ingredients resulting from the reactions, principally sulfides of calcium and sodium. In order to obtain it in a condition suitable for trade, LeBlanc soda must undergo a rather tedious and costly process of purification; and if it were not for the by-products obtained during the process, the product would be too expensive for use.[4] Solvay soda is prepared by conducting a mixture of ammonia and carbon dioxide gases through a concentrated brine solution. This results in the formation of sodium bicarbonate and ammonium chloride: the former being insoluble in the salt solution, is precipitated and thus collected. The ammonia is recovered from the ammonium chloride and is used over continuously with but small loss. The sodium bicarbonate is readily converted into the plain carbonate by calcining. Solvay soda, if properly prepared, is a very pure article, and can be produced quite cheaply. It is not liable to contamination with iron or aluminium, as is the case with LeBlanc soda. The fact that soda ash can be obtained in such a high degree of purity has caused the use of sal soda to diminish very considerably, as the latter for the same weight has only about one-third as much alkali as the former.

The strength of sodium carbonate (of whatever variety) is usually based on the amount of "pure alkali" or sodium oxide, Na_2O, it contains. The percentages of this are expressed in terms of degrees; for instance, "48° alkali" would indicate that the sample contained 48 percent of Na_2O. Chemically pure sodium carbonate, Na_2CO_3, would correspond to 58.5° alkali.[5] Good qualities of soda ash when dissolved in water should leave little or no residue. The chief impurities which may be present are the chloride, sulfate, sulfite, and sulfide of sodium, free caustic alkali, lime, iron, alumina, and silica.

[4] Le Blanc soda is very liable to contain as impurities small amounts of caustic soda and sodium sulfide. The presence of the latter may be indicated by testing with lead acetate paper, which gives a brown or black color due to the formation of lead sulfite A good sample of soda should be soluble in water with not more than a trace of insoluble residue (sand and carbon)

[5] In France, soda ash is generally valued in terms of what is called the Descroizilles degree; this degree represents the number of parts by weight of monohydrated sulfuric acid which can be neutralized by 100 parts of the sample being tested. Pure sodium carbonate titrates 92.45 degrees Descroizilles. In analyzing samples of soda ash on this basis the standard acid is made up so that 92.45 c.c. exactly neutralizes 10 gms. of pure sodium carbonate. The strength of alkali may also be expressed in terms of the Gay-Lussac degree, which refers to the percentage strength of the alkali in anhydrous caustic soda, calculated from the atomic weight of 62. The English degree also expresses this same factor, but based on the old atomic weight of 64. Newcastle alkali is sold on the Gay-Lussac standard and the Liverpool alkali on the English standard The German degree alkali represents the percentage of sodium carbonate. The following table presents the relation of the values of these different degrees of alkaline strength:

Descroizilles	German	Gay-Lussac	English
1.000	1.081	0.632	0.641
0.924	1.000	0.585	0.592
1.580	1.709	1.000	1.013
1.560	1.687	0.987	1.000

The following tables show the density of solutions of soda ash:

DENSITIES OF SOLUTIONS OF SODA ASH (AT 60° F.)

TABLE I

Degrees Twaddell	Percentage by Wt.		Degrees Twaddell	Percentage by Wt.	
	Na_2CO_3	Na_2O		Na_2CO_3	Na_2O
1	0.47	0.28	16	7.57	4.42
2	0.95	0.56	17	8.04	4.70
3	1.42	0.84	18	8.51	4.97
4	1.90	1.11	19	8.97	5.24
5	2.38	1.39	20	9.43	5.52
6	2.85	1.67	21	9.90	5.79
7	3.33	1.95	22	10.37	6.06
8	3.80	2.22	23	10.83	6.33
9	4.28	2.50	24	11.30	6.61
10	4.76	2.78	25	11.76	6.88
11	5.23	3.06	26	12.23	7.15
12	5.71	3.34	27	12.70	7.42
13	6.17	3.61	28	13.16	7.70
14	6.64	3.88	29	13.63	7.97
15	7.10	4.16	30	14.09	8.24

TABLE II

Sp. Gr.	°Bé	Na_2CO_3 Percent	$Na_2CO_3.10H_2O$ Percent	Kilos. in one Cu. Meter	
				Na_2CO_3	$Na_2CO_3.10H_2O$
1.007	1	0.67	1.81	6.8	18.2
1.014	2	1.33	3.59	13.5	36.4
1.022	3	2.09	5.64	21.4	57.6
1.029	4	2.76	7.44	28.4	76.6
1.036	5	3.43	9.25	35.5	95.8
1.045	6	4.29	11.57	44.8	120.9
1.052	7	4.94	13.32	52.0	140.2
1.060	8	5.71	15.40	60.5	163.2
1.067	9	6.37	17.18	68.0	183.3
1.075	10	7.12	19.20	76.5	206.4
1.083	11	7.88	21.25	85.3	230.2
1.091	12	8.62	23.25	94.0	253.6
1.100	13	9.43	25.43	103.7	279.8
1.108	14	10.19	27.48	112.9	304.5
1.116	15	10.95	29.53	122.2	329.6
1.125	16	11.81	31.85	132.9	358.3
1.134	17	12.61	34.01	143.0	385.7
1.142	18	13.16	35.49	150.3	405.3
1.152	19	14.24	38.41	164.1	442.4

At the present time, soda ash of both the LeBlanc and Solvay manufacture is brought into trade in a high degree of purity; this was necessitated by the fact that soda ash employed in the scouring of textile materials previous to dyeing should be as free as possible from contamination with salts of iron, the presence of which metal rendering it almost impossible to obtain clear bright shades with many dyes,

and more especially the alizarine or mordant colors. The presence of iron also caused uneven streaks and spots to appear in the dyeing. The yellowish tinge to be noticed in many samples of soda ash is not always to be attributed to the presence of iron compounds, as it is usually caused by a slight amount of organic matter which cannot be considered as objectionable. Caustic soda is another impurity which is liable to occur in soda ash, and for many purposes, especially those pertaining to the scouring of wool, it is objectionable. This impurity is more liable to be present in LeBlanc soda; seldom, if ever, being found in samples of Solvay soda; the latter on the other hand is apt to contain small quantities of sodium bicarbonate, the occurrence of which insures the absence of caustic soda, and is not objectionable, except in so far as it somewhat lowers the alkaline strength of the compound.

Sodium and potassium carbonates are largely used for scouring, and in connection with their respective soaps are the cheapest and most popular detergents in use. Both the carbonated alkali and the soap employed should be of the best quality consistent with the cost of scouring. Neither one should contain any appreciable amount of caustic alkali, as this latter substance rapidly destroys the wool fiber, even in dilute solutions and at moderate temperatures. A good olive oil soap is considered to be the best for ordinary scouring; either a hard (soda) or soft (potash) soap being used. Although a neutral soap is to be recommended, nevertheless, a great deal of scouring is done with soaps and alkalies containing quite an appreciable amount of free caustic alkali. As wool-fat contains a good proportion of free acid, it is possible to do this at times without material injury to the fiber, since the caustic alkali will generally combine with the free fatty acid before it has a chance to act on the material of the wool itself. Such a procedure, no doubt, considerably expedites the scouring, but is dangerous unless carried out in a skillful and experienced manner, especial attention being given to the proper regulation of the temperature of the bath, and it is not to be recommended in general practice.

The use of patented scouring powders and secret soap preparations is also to be avoided, unless their reliability is unquestionable and their composition and characteristics understood. Many of these contain relatively large amounts of caustic alkali.

The addition of ammonia or ammonium carbonate to the scouring baths is beneficial, and where the expense is justified is said to yield better results than the other alkalies. Owing to their volatility, ammonium compounds are easily removed from the fiber after scouring, and their use involves less danger of felting.

3. Qualitative Analysis of Soda Ash.

(a) *Iron.*—Dissolve a small quantity of the sample in pure dilute nitric acid; after effervescence has ceased add a drop or two of concentrated nitric acid and boil for a few minutes. On cooling, add a few drops of a solution of potassium sulfocyanide to one portion of the solution, when the formation of a red color will indicate the presence of iron. To the other portion add a few drops of a solution of

potassium ferrocyanide, when the formation of a blue color will indicate the presence of iron and thus confirm the first test.

(b) *Sodium Chloride.*—Dissolve a small quantity of the sample in pure dilute nitric acid, and after effervescence has ceased, boil the solution for a few minutes to expel the carbon dioxide gas, then add a few drops of a solution of silver nitrate, when the formation of a white precipitate or cloudiness will indicate the presence of sodium chloride.

(c) *Sodium Sulfate.*—Dissolve a small quantity of the sample in pure dilute nitric acid as before, and after expelling carbon dioxide gas by boiling, add a few drops of a solution of barium chloride, when the formation of a white precipitate or cloudiness will indicate the presence of sodium sulfate.

(d) *Sodium Sulfate.*—Dissolve a small quantity of the sample in water, and place in the solution a strip of filter paper saturated with lead acetate solution. If an appreciable amount of sodium sulfide is present, the paper will become brown in color, due to the formation of lead sulfide. A more delicate test is to dip a strip of filter paper saturated with sodium nitroprusside solution into the solution of soda ash, when the formation of blue violet color on the paper will indicate the presence of sodium sulfide If the soda ash is contaminated to any extent with sodium sulfide, the odor of hydrogen sulfide will be noticed on dissolving the sample in acid.

(e) *Caustic Soda.*—Dissolve a small quantity of the sample in water and add a solution of barium chloride until no further precipitate is formed. This will cause the precipitation of all sodium carbonate present, but will still leave any caustic soda in solution. After allowing the precipitate to settle, filter, and add to the filtrate a few drops of phenolphthalein solution, when the formation of a red or violet color will indicate the presence of caustic soda in the original sample.

(f) *Lime.*—Dissolve a small quantity of the sample in water, and add a few drops of a solution of ammonium oxalate, when a white precipitate or cloudiness will be formed if lime is present.

(g) *Bicarbonate.*—Place a small quantity of the sample in a test tube and heat it in a bunsen flame, leading the gases that may be evolved through lime water. The formation of a cloudiness in the lime water will indicate the presence of bicarbonate in the sample.

4. Quantitative Analysis of Soda Ash.[6]

(a) *Total Alkali.*—Weigh out accurately about 1 gm. of the sample and dissolve in hot water; after cooling, make up the solution

[6] The following are representative analyses of typical samples of soda ash:

Le Blanc Soda	Percent	Solvay Soda	Percent
Sodium carbonate	86.42	Sodium carbonate	98.72
Sodium hydrate	nil	Sodium chloride	0.54
Sodium chloride	7 40	Sodium sulfate	0.20
Sodium sulfate	3.62	Magnesium carbonate	0.04
Alumina	0.14	Calcium carbonate	0.13
Ferric oxide	0.03	Ferric oxide	0.01
Sodium silicate	0.51	Alumina	0 01
Insoluble matter	0.05	Silica	0.09
Water	1.77	Water	0.32

to one liter. Measure out 25 cc. with a pipette into a small flask and add a few drops of Methyl Orange, then titrate with 1/10-normal sulfuric acid until the yellow color of the Methyl Orange is turned to a reddish tone. Each c.c. of 1/10-normal acid used corresponds to 0.0031 gm. pure alkali, Na_2O, or to 0.0053 gm. sodium carbonate, Na_2CO_3.

Example.—Sample of soda ash taken weighed 1.000 gm. Dissolved in water and diluted to one liter; 25 c.c. of this solution on titration with 1/10-normal sulfuric acid required 4.3 c.c. for neutralization. As a liter (1000 c.c.) of the soda ash solution contained 1 gm., 25 c.c. would contain 0.025 gm., and as each c.c. of acid is equivalent to 0.0053 gm. of sodium carbonate, there would be present 0.02279 gm. of the latter, which would be 91.2 percent. If it is desired to calculate it as "pure alkali," 4.3 c.c. of acid would correspond to 0.01333 gm. Na_2O, or 53.3° alkali.

(b) *Caustic Soda and Sodium Carbonate.*—Take 100 c.c. of the above solution of the sample, and add a few drops of a solution of phenolphthalein, and titrate with 1/10-normal sulfuric acid until the red color of the phenolphthalein is discharged. This reaction will indicate that all of the caustic soda present has been neutralized together with one-half of the sodium carbonate, because the phenolphthalein is sensitive to free carbonic acid, and its color will be discharged when all of the sodium carbonate has become changed into bicarbonate and a trace of free carbonic acid is liberated. The number of c.c. of acid required for this reaction is noted. Then a few drops of Methyl Orange solution are added, and the titration with the acid is continued until the appearance of a reddish tint shows that the rest of the alkali is neutralized. The quantity of acid necessary for the second titration corresponds to one-half of the sodium carbonate, so this is multiplied by two to give the amount of sodium carbonate actually present. The difference between the amounts of acid added for the first and second titrations corresponds to the amount of caustic soda present. Each c.c. of 1/10-normal sulfuric acid is equivalent to 0.0053 gm. of sodium carbonate, Na_2CO_3, and to 0.0040 gm. of caustic soda, NaOH.[7]

Example.—100 c.c. of the solution of soda ash titrated as above directed, required for the first titration 8.9 c.c., and for the second titration 8.3 c.c. of acid. Hence, we have as follows:

$8.3 \times 2 = 16.6 \times 0.0053 = 0.08798$ gm. sodium carbonate, which is equivalent to 87.98 percent.

$8.9 - 8.3 = 0.6 \times 0.0040 = 0.0024$ gm. caustic soda, which is equivalent to 2.4 percent.

As in technical analysis it is more customary to state the amounts of carbonate and hydrate in terms of "alkali" Na_2O, the above amounts become in this form (since each c.c. of 1/10-normal acid is equivalent to 0.0031 gm. of Na_2O):

[7] Another method for determining the amount of caustic soda in a sample of soda ash is the following: Take 250 c.c. of the soda ash solution (10 gms. per liter) and place in a 500 c.c. graduated flask; add a slight excess of a neutral solution of barium chloride, and fill the flask to the mark with distilled water: All of the carbonate present will be precipitated as barium carbonate. This is allowed to settle and then 200 c.c. of the clear supernatant liquid (equivalent to 1 gm of the sample) are withdrawn and titrated with 1/10 normal sulfuric acid, using either phenolphthalein or Methyl Orange as indicators. Each c.c. of acid required is equivalent to 0.0031 gm. Na_2O or 0.0040 gm. of caustic soda Instead of using sulfuric acid for the titration, oxalic acid may be employed; in which case the liquid containing the precipitated barium carbonate may be directly titrated without waiting for the precipitate to settle.

16.6 x 0.0031 = 0.05146 gm. alkali as carbonate, and this would be equal to 51.46°.
0.6 x 0.0031 = 0.00186 gm. alkali as caustic, and this would be equal to 1.86°.

(c) *Insoluble Matter.*—Weigh out accurately 10 gms. of the sample, and dissolve in about one liter of hot water; filter, and wash the filter well with water; then dry the filter, ignite in a porcelain crucible and weigh. This will give the amount of insoluble mineral matter present in the sample.

Example.—10 gms. of soda ash treated as above gave the following results:

Weight of crucible empty	15.125 gms.
Weight with ignited residue	15.167 gms.
Weight of insoluble matter .	0.042 gm.

and this is equivalent to 0.4 percent

(d) *Sodium Sulfate.*—The preceding solution of 10 gms. of the sample is made to just 1000 c.c. after filtration. 200 c.c. of this solution (corresponding to 2 gms. of soda ash) are slightly acidulated with hydrochloric acid and boiled until all carbon dioxide gas is removed; then a solution of barium chloride is added in slight excess, which will cause the precipitation of all sodium sulfate present as barium sulfate. After setting the barium sulfate is filtered off, washed, dried, ignited in a porcelain crucible, and weighed. One part of barium sulfate corresponds to 0.609 part of sodium sulfate.[8]

Example.—200 c.c. of the above solution treated as described, gave the following results:

Weight of crucible empty .	15.125 gms.
Weight with barium sulfate .	15.136 gms
Weight of barium sulfate . . .	0.011 gm

This corresponds to 0.011 x 0.609 = 0.0067 gm sodium sulfate, which is equivalent to 0.32 percent.

(e) *Sodium Chloride.*—This may be best estimated volumetrically by the use of 1/10-normal solution of silver nitrate with potassium chromate as an indicator. The 1/10-normal solution of silver nitrate may be prepared by dissolving 16.966 gms. of the pure salt in water and diluting to just one liter. Each c.c. of this solution is equivalent to 0.00355 gm. chlorine or 0.00585 gm. sodium chloride. 100 c.c. of the same solution of soda ash as used in the previous determination are just neutralized with nitric acid in a porcelain dish and a few drops of a solution of potassium chromate are added. The liquid is then titrated with the silver nitrate solution until the color becomes a faint orange, which indicates all of the chloride present has combined with the silver salt.

Example.—100 c.c. of the soda ash solution (equivalent to 1 gm.) was titrated as above described and required 1.2 c.c. of 1/10-normal silver nitrate solution. This was equal to 1.2 x 0.00585 = 0.00702 gm. of sodium chloride, or 0.70 percent.

[8] Other compounds of sulfur than the sulfate are not liable to occur in samples of good soda ash. Should they be present, however, they may be estimated by adding to 50 c.c. of the soda ash solution a solution of barium hypochlorite, then adding hydrochloric acid to dissolve the precipitated barium carbonate; boil well, filter off the residual precipitate of barium sulfate, dry, ignite, and weigh. The difference between the first determination of free sulfate and the latter will give the amount of sulfur compounds other than sodium sulfate. As these compounds consist chiefly of sulfides, sulfites, etc., they are all oxidized to the form of sulfate by the action of the hypochlorite.

(f) *Sodium Sulfide.*—The amount of sodium sulfide present in a sample of soda ash may be determined by titration with a standard solution of ammoniacal silver nitrate. This solution is prepared by dissolving 21.792 gms. of pure silver nitrate in water, and adding 250 c.c. of ammonia, and making up to one liter; 1 c.c. of this solution is equivalent of 0.005 gm. of sodium sulfide. The titration is carried out by taking 100 c.c. of the soda ash solution similar to the preceding (equivalent to 1 gm. of soda ash sample), adding some ammonia water, and heating to boiling. The silver nitrate solution is then run in until no further precipitation of silver sulfide occurs. The exact point at which this occurs can best be determined by filtering a few drops of the liquid, and testing the clear filtrate with a drop of silver nitrate solution.[9]

Example.—100 c.c. of the soda ash solution titrated in the manner as above described gave the following results: 0.3 c.c. of the ammoniacal silver nitrate solution were required for the titration; hence 0.005 x 0.3 = 0.0015 gm. sodium sulfide, or 0.15 percent.

(g) *Sodium Sulfite.*—This component is determined together with sodium sulfide by titration with a 1/10-normal solution of iodine. To 100 c.c. of the soda ash solution (10 gms. per liter) add a slight excess of acetic acid and a little starch solution. Titrate with iodine solution until a blue color is developed. Each c.c. of the 1/10-normal iodine solution is equivalent to 0.0039 gm. of sodium sulfide and to 0.0063 gm. of sodium sulfite; so calculate the quantity of the iodine solution equivalent to the amount of sodium sulfide found in the above test and subtract from the total c.c. of iodine solution used, and from the remainder calculate the quantity of sodium sulfite.

Example.—100 c.c. of the solution of soda ash (equivalent to 1 gm.) required 0.6 c.c. of 1/10-normal iodine solution for titration; as there was found to be 0.0015 gm. of sodium sulfide in this amount of the sample, this was equivalent to 0.4 c.c. of the iodine solution, consequently, 0.2 c.c. corresponded to the amount of sodium sulfite present, or 0.2 x 0.0063 = 0.00126 gm., or 0.12 percent.

Neither sodium sulfide nor sodium sulfite is liable to be found in samples of soda ash unless the same are rather crude.

(h) *Oxides of Iron and Aluminium.*—The mixed oxides of iron and aluminium are estimated by dissolving 5 gms. of the sample in water, filtering and washing the residue on the filter paper until the washings are neutral to litmus. An excess of hydrochloric acid and a few drops of nitric acid are added to the filtrate, and the solution, after boiling, is precipitated by the addition of a slight excess of ammonia. Filter, wash the precipitate; dry, ignite and weigh. This will give the amount of the mixed oxides of iron and aluminium.

To determine the amount of *iron,* dissolve about 5 gms. of the sample of soda ash in water in a flask, add a small quantity of dilute sulfuric acid, and boil until carbon dioxide or other gases are ex-

[9] Another method for determining the amount of sodium sulfide is the following: Prepare a solution of lead nitrate containing 4.25 gms. per liter; each c.c. of this solution will be equivalent to 0.001 gm. of sodium sulfide. Take 50 c.c. of the soda ash solution (10 gms per liter) and titrate with the lead nitrate solution. As an indicator, place a few drops of the lead nitrate solution on a piece of filter paper; occasionally remove from the liquid undergoing titration a drop on the end of a glass rod and add it to the drop of lead nitrate solution on the filter paper; when the latter ceases to give a dark coloration, the titration is completed.

pelled. Then add a small fragment of mossy zinc which will cause the reduction of any iron present to the ferrous condition. The solution is then titrated with a N/50 solution of potassium permanganate, each c.c. of which is equivalent to 0.00112 gm. of iron or to 0.0016 gm. of ferric oxide, Fe_2O_3.[10] By subtracting the latter amount from the quantity of the mixed oxides found as above described, the amount of *alumina* may be determined.

(i) *Lime*.—This may be determined by taking the filtrate from the mixed oxides of iron and aluminium described above, concentrating to a small bulk, and adding a solution of ammonium oxalate. The calcium oxalate which is precipitated is collected on a filter, washed, dried, ignited, and then a drop of sulfuric acid is added and the mass ignited again, and finally weighed as calcium sulfate; 1 part of the latter is equivalent to 0.41 part of lime, CaO.[11]

5. Potassium Carbonate.

This is the potassium compound corresponding to soda ash, and it has the chemical formula K_2CO_3. As potassium salts do not occur as largely in nature as the sodium salts, the former are always more expensive. Potassium carbonate is also called *potash* and *pearl ash*. Formerly it was principally obtained from the ashes of land plants; and, in fact, it received its name from "pot ashes," meaning the ashes left after burning wood under the pots. At the present time potash is chiefly obtained from the potassium salts mined at Strassfurt in Germany, and in Alsace, France, although a large quantity is still produced locally by extracting wood ashes with water. Potash, as it appears in trade, is a white granular substance which rapidly absorbs moisture from the air, and becomes pasty in consistency. It also occurs at times in the crystalline condition, the crystals having the formula $K_2CO_3 \cdot 1\frac{1}{2}H_2O$. In its chemical properties potash very much resembles soda ash; it is much more soluble than the latter, however, and it does not appear to have such a severe action on wool as soda ash. Potash is largely used for the making of soft soaps, and somewhat for the scouring of high grade wool; although for this purpose it is considerably more expensive than soda ash.

[10] When the amount of iron present in a sample of soda ash is very small, it will be difficult to obtain satisfactory results by the gravimetric method, and the following colorimetric method is proposed. Dissolve 10 gms. of the soda ash in hydrochloric acid, add a few drops of nitric acid and boil to insure the complete oxidation of all the iron to the ferric condition and the removal of all the carbon dioxide from the solution. Then pour the solution into a narrow glass cylinder, and add 2 c.c. of a 10 percent solution of ammonium sulfocyanide, which will give a red coloration with the iron. In a similar glass cylinder, place 25 c.c. of hydrochloric acid and a few drops of nitric acid, then dilute with water until the volume is the same as that of the soda ash solution; then add 2 c.c. of ammonium sulfocyanide solution and titrate with a solution of ferric chloride containing 1 gm. of iron per liter, until the depth of color in the second glass is the same as that in the first. In this manner the amount of iron in the soda ash solution may be readily calculated, as each c.c. of the ferric chloride solution will be equivalent to 0.001 gm. of iron or 0.00285 gm. of ferric oxide, Fe_2O_3.

[11] It is sometimes desirable to ascertain the amount of silica in a sample of soda ash, and this may be done in the following manner: Dissolve 10 gms. of the soda ash in hydrochloric acid; evaporate the solution to dryness in a casserole on a water-bath; dissolve the dry residue in water containing a few drops of hydrochloric acid; filter off the insoluble portion; dry, ignite, and weigh as silica, SiO_2. This amount multiplied by the factor 2.03 will give the equivalent of sodium silicate.

STRENGTH OF POTASSIUM CARBONATE SOLUTIONS

Bé.°	Tw.°	Percent K_2CO_3.	Gms. per liter of K_2CO_3	Bé.°	Tw.°	Percent K_2CO_3.	Gms. per liter of K_2CO_3.
2	2.8	1.5	15	28	48.2	24.5	304
4	5.8	3.1	32	30	52.6	26.6	336
6	9.0	4.9	51	32	57.0	28.5	366
8	12.0	6.5	69	34	61 6	30.7	402
10	15.0	8.1	87	36	66.4	32.7	436
12	19.2	9.8	107	38	71.4	34.8	472
14	21.6	11.6	129	40	76 6	37.0	512
16	25.0	13.3	150	42	82.0	39.3	554
18	28.4	15.0	171	44	87.6	41.7	600
20	32.4	17.0	198	46	93 6	44.0	646
22	36 0	18.8	222	48	99.6	46.5	697
24	40 0	20.7	248	50	106 0	48.9	748
26	44 0	22.5	275	52	112.0	51.3	802

Potash is analyzed in general in the same manner as soda ash; usually, the only components determined are the potassium carbonate, caustic potash, and water. The latter is obtained by simply drying a sample at 110° C. until constant weight is obtained.[12]

6. Caustic Soda.

Caustic soda is chemically known as sodium hydrate and has the formula NaOH. It is a white brittle substance and absorbs moisture eagerly from the air, so that if left exposed for any length of time, it soon becomes liquefied. It is very soluble in water, and on dissolving liberates considerable heat; its solution in water is generally known as soda lye.[13] Caustic soda is a very strong alkali and is very caustic in its properties. It will cause severe burns if in contact with the skin, so workmen handling caustic soda should have their hands protected with rubber gloves. Caustic soda is mostly prepared by a double decomposition between sodium carbonate and caustic lime, whereby carbonate of lime and caustic soda are formed. It is also made by the action of oxide of iron on sodium carbonate, and quite largely at the present time by the electrolysis of brine solutions whereby chlorine and caustic soda are formed. Caustic soda is usually sold on a

[12] The following are analyses of typical samples of commercial potash:

	Montreal	Pearlash	French	Beetroot	LeBlanc
Potassium carbonate	43 87	77 50	38 63	92.68	92 19
Potassium sulfate	10 40	11 65	0 43	3 81	3.94
Potassium hydroxide	36 50	....	....	....	....
Potassium chloride	2.40	2.65	2 45	2 92	1.49
Sodium carbonate	....	2 86	3 98	3 98	1 43
Sodium hydroxide	2 03	....	4.17	....	....
Soluble silica, etc.	4 75	5.77	9 20	0.56	1.08

[13] One part of caustic soda dissolves in 0 47 part of water, and the greatest amount of heat of solution is liberated when 1 part of caustic soda is dissolved in 90 parts of water, these proportions corresponding to the ratio of NaOH $20H_2O$. The following table shows the relation between the strength of caustic soda solutions and their boiling points.

Percent NaOH	Boiling Point C°.	F°.
36	130	266
70	180	356
78	243	469
82	260	500

basis of its percentage of sodium oxide (Na_2O); each percent being expressed as a degree. Thus 77° caustic soda would mean that it contains 77 percent of sodium oxide, and would be almost chemically pure. Caustic soda is used very largely in the scouring and bleaching of cotton and for the preparation of soaps. The lower grades of caustic soda are usually sold in iron drums, which are filled with the melted caustic soda and hermetically sealed; the higher grades are generally sold in the powder form. Caustic soda may also be purchased in the form of a solution, the usual commercial article having a density of 1.35 or 70° Tw., and containing about 30 percent of actual caustic soda. It is also sold at a density of 100° Tw., containing about 50 percent of caustic soda.

STRENGTH OF CAUSTIC SODA SOLUTIONS

Bé.°	Tw.°	Percent Na_2O.	Percent NaOH.	Tw.°	Bé.°	Percent Na_2O.	Percent NaOH.
1	1.4	0.47	0.61	26	44.0	15.18	19.58
2	2.8	0.93	1.20	27	46.2	15.96	20.59
3	4.4	1.55	2.00	28	48.2	16.76	21.42
4	5.8	2.10	2.71	29	50.4	17.55	22.64
5	7.2	2.60	3.35	30	52.6	18.35	23.67
6	9.0	3.10	4.00	31	54.8	19.23	24.81
7	10.4	3.60	4.64	32	57.0	20.00	25.80
8	12.0	4.10	5.29	33	59.4	20.80	26.83
9	13.4	4.55	5.87	34	61.6	21.55	27.80
10	15.0	5.08	6.55	35	64.0	22.35	28.83
11	16.6	5.67	7.31	36	66.4	23.20	29.93
12	18.2	6.20	8.00	37	69.0	24.20	31.22
13	20.0	6.73	8.68	38	71.4	25.17	32.47
14	21.6	7.30	9.42	39	74.0	26.12	33.69
15	23.2	7.80	10.06	40	76.6	27.10	34.96
16	25.0	8.50	10.97	41	79.4	28.10	36.25
17	26.8	9.18	11.84	42	82.0	29.05	37.47
18	28.4	9.80	12.64	43	84.8	30.08	38.80
19	30.4	10.50	13.55	44	87.6	31.00	39.99
20	32.4	11.14	14.37	45	90.6	32.10	41.41
21	34.2	11.73	15.13	46	93.6	33.20	42.83
22	36.0	12.33	15.91	47	96.6	34.40	44.38
23	38.0	13.00	16.77	48	99.6	35.70	46.15
24	40.0	13.70	17.67	49	102.8	36.90	47.60
25	42.0	14.40	18.58	50	106.0	38.00	49.02

7. Analysis of Caustic Soda.[14]

The strength of caustic soda (either as the solid or in the form of solution) is determined by titration of a definite quantity of the sample with 1/10-normal acid as in the case of soda ash; each c.c. of 1/10-

[14] The following are analyses of typical samples of caustic soda, known as 70, 72, and 78 percent, the latter being made by the electrolytic method:

	70 Percent	72 Percent	78 Percent
Sodium hydrate	86.70	87.94	99.22
Sodium carbonate	3.25	4.74	nil
Sodium sulfate	2.90	4.88	0.13
Sodium chloride	6.87	2.02	0.65
Sodium silicate	0.10	0.15	0.03
Sodium sulfide	nil	nil	nil
Alumina	0.09	0.04	0.003
Insoluble	nil	nil	nil
Moisture	0.20	nil	nil

normal sulfuric acid is equivalent to 0.0040 gm. of NaOH or 0.0031 gm. of Na_2O if the analysis is to be expressed in degrees of alkali. To test for the presence of sodium carbonate in a sample of caustic soda, dissolve in water and add a few drops of hydrochloric acid (or the acid may be added directly to the solid caustic soda) and if an effervescence is noticed, sodium carbonate is present. The amount of sodium carbonate and sodium hydrate in a sample may be determined by titration with 1/10-normal sulfuric acid, using phenolphthalein first as the indicator and then continuing the titration with Methyl Orange as the indicator, as explained under the analysis of soda ash. The number of c.c. of acid required for the latter titration represents one-half of the sodium carbonate present.

Example.—1 gm. of a sample of caustic soda was dissolved in water and the solution made up to one liter; 100 c.c. of this solution were withdrawn and titrated with 1/10-normal sulfuric acid using phenolphthalein as an indicator; it required 10.4 c.c. for neutralization. A few drops of Methyl Orange were added and the titration continued; it required 1.7 c.c. for further neutralization. Hence as each c.c. of 1/10-normal sulfuric acid is equivalent to 0.0053 gm. of sodium carbonate, and as the second titration corresponds to one-half the carbonate, we have 1.7 x 0.0053 x 2 = 0.018 gm. of sodium carbonate, or 18 percent. As the first titration represented all of the caustic soda and one-half of the carbonate, we have, 10.4 — 1.7 = 8.7 c.c. of acid corresponding to the caustic soda; and this is equivalent to 8.7 x 0.0040 = 0.0348 gm., or 34.8 percent of caustic soda.

Example.—How many ounces of true caustic soda are contained in a gallon of a soda lye which analyzed as follows: 100 c.c. of the lye were diluted to one liter, and 100 c.c. of this solution required on titration on phenolphthalein 32.6 c.c. of 1/10-normal acid, and on further titration on Methyl Orange, 0.8 c.c.?

0.8 x 2 x 0.0053 = 0.00848 gm. of sodium carbonate;

32.6 — 0.8 = 31.6 x 0.0040 = 0.1264 gm. of caustic soda.

As 100 c.c. of the diluted solution taken for titration represented 10 c.c. of the actual lye, there would be in one liter of the lye 0.848 gm. of sodium carbonate and 12.64 gms. of caustic soda. As a U. S. gallon contains 3.78 liters, this would be 47.78 gms. of caustic soda per gallon, or as one ounce contains 28.35 gms., this would be 1.68 ozs. per gallon. The factor for converting accurately gms. per liter into ozs. per gallon (U. S.) is 0.133; that is, taking the above example, we have: 12.64 gms. per liter x 0.133 = 1.68 ozs. per gallon.

8. Sodium Silicate.

This alkali finds some application in scouring and bleaching, although it is not as advantageous as a rule as soda ash or caustic soda.[15] Sodium silicate is also known as water-glass, and appears in trade mostly in the form of a thick syrupy solution, though it may also be obtained as a solid in lump form.[16] The addition of acids decomposes solutions of sodium silicate with the precipitation of gelatinous silica;

[15] An investigation of the use of sodium silicate in scouring is given in *Deutsche Farb Zeit.*, 1885, No. 3, a summary of which may be given as follows: For linen cloth sodium silicate was found to be far superior to soap, for wool the contrary is the case, and for cotton it is not so advantageous; less work is required when it is used than when soap is employed. Sodium silicate is much cheaper than soap; on linen cloth the combined use of sodium silicate and soap produces better results as regards color and strength than with soap alone; for the scouring of half-woolen goods preparatory to bleaching, soda ash is better and cheaper to use than sodium silicate; and in the bleaching of cotton soap is superior, as the latter not only cleanses but also gives the fabric a softer feel.

[16] Sodium silicate is extensively employed as a filler for cheap and low-grade soaps. A soap containing a large amount of sodium silicate may appear hard and dry and yet contain a high proportion of water, owing to the colloidal character of the silicate and its ability to form a solid mass with a large amount of water.

the addition of many metallic salts also has a like action. Solutions of sodium silicate react strongly alkaline.

Sodium silicate is rather extensively used in the preparation of "bleacher's assistants" to be used in the boiling-out of cotton in the kier. It also finds favor with a number of bleachers as an addition to the kier-boil in connection with caustic soda and soda ash. It is said to give the goods a softer feel.

9. Caustic Potash.

Caustic Potash corresponds to sodium hydrate and is very similar to it in its properties. It is made by the double decomposition between potash and lime in the same manner as caustic soda. Caustic potash is used in the manufacture of soft soaps, but for other purposes it is replaced by the cheaper sodium compound. Caustic potash is analyzed in the same manner as the sodium salt, each c.c. of 1/10-normal acid being equivalent to 0.0056 gm. KOH, or 0.0047 gm. K_2O, or 0.0069 gm. K_2CO_3 The best quality of caustic potash usually contains from 80 to 85 percent of actual potassium hydroxide; the next quality contains from 75 to 80 percent, while the poorest quality contains from 70 to 75 percent.[17] A higher grade caustic potash has recently been prepared by an electrolytic process and at a cost which should make it commercially available.

The impurities in commercial caustic potash, as a rule, are a good deal higher than those in caustic soda; it is also difficult to obtain the former free from considerable amounts of the caustic soda. The amounts of potassium carbonate, potassium chloride, potassium sulfate, alumina, etc., are obtained in the same manner as described under the analysis of caustic soda. The estimation of the amount of caustic soda present is rather difficult, as it is hard to obtain a clean and easy analytical separation of sodium compounds from those of potassium. The best method is probably to determine the amount of potassium present by means of platinum chloride, and then to calculate the soda by difference between the sulfuric acid required for the potassium so found and that used for the total alkalinity of the sample. This estimation is carried out in the following manner: 5 gms. of the sample are dissolved in water, and the solution diluted to 500 c.c. After standing for some time to allow the deposition of any insoluble matter, 25 c.c. are withdrawn and transferred to a porcelain dish; a slight excess of hydrochloric acid is added, and then an excess of platinum chloride, $PtCl_4$. The solution is then evaporated nearly to dryness on a water bath, and if the liquid does not remain of a dark

[17] The following are analyses of two typical samples of commercial caustic potash:

	Percent No 1	Percent No 2
Potassium hydroxide	77 64	75 64
Potassium carbonate	4 62	2 55
Potassium sulfate	0 38	0 21
Potassium chloride	2 29	0 93
Potassium nitrite	0 87	nil
Sodium hydroxide	4 67	2 59
Soluble silica and alumina	0 30	0 20
Insoluble matter	0 02	0.22
Water	8 84	17 80

yellow color during the evaporation, more platinum chloride is added. To the semi-solid residue add some pure alcohol and mix the contents well; allow the precipitate to settle, and pour off the liquid through a tared filter. Repeat the washing with alcohol twice, and finally transfer the insoluble double salt of potassium and platinum chloride to the filter, and wash with alcohol until the washings are no longer colored yellow; then dry the filter and its contents at 100° C. and weight as $PtCl_4.2KCl$. The weight of this salt multiplied by the factor 0.161 will give the amount of potassium present; or by the factor 0.194 will give the amount as potassium oxide, K_2O; or by the factor 0.231 will give amount as potassium hydroxide, KOH.

STRENGTH OF CAUSTIC POTASH SOLUTIONS (I)

Bé.°	Tw.°	Percent K_2O.	Percent KOH.	Bé.°	Tw.°	Percent K_2O.	Percent KOH.
1	1.4	0.7	0.9	29	50.4	22.7	27.0
2	2.8	1.4	1.7	30	52.6	23.5	28.0
3	4.4	2.2	2.6	31	54.8	24.2	28.9
4	5.8	2.9	3.5	32	57.0	25.0	29.8
5	7.4	3.8	4.5	33	59.4	25.8	30.7
6	9.0	4.7	5.6	34	61.6	26.7	31.8
7	10.4	5.4	6.4	35	64.0	27.5	32.7
8	12.0	6.2	7.4	36	66.4	28.3	33.7
9	13.4	6.9	8.2	37	69.0	29.3	34.9
10	15.0	7.7	9.2	38	71.4	30.2	35.9
11	16.6	8.5	10.1	39	74.0	31.0	36.9
12	18.2	9.2	10.9	40	76.6	31.8	37.8
13	20.0	10.1	12.0	41	79.4	32.7	38.9
14	21.6	10.8	12.9	42	82.0	33.5	39.9
15	23.2	11.6	13.8	43	84.8	34.4	40.9
16	25.0	12.4	14.8	44	87.6	35.4	42.1
17	26.8	13.2	15.7	45	90.6	36.5	43.4
18	28.4	13.9	16.5	46	93.6	37.5	44.6
19	30.4	14.8	17.6	47	96.6	38.5	45.8
20	32.4	15.6	18.6	48	99.6	39.6	47.1
21	34.4	16.4	19.5	49	102.8	40.6	48.3
22	36.0	17.2	20.5	50	106.0	41.5	49.4
23	38.0	18.0	21.4	51	109.2	42.5	50.6
24	40.0	18.8	22.4	52	112.6	43.6	51.9
25	42.0	19.6	23.3	53	116.0	44.7	53.2
26	44.0	20.3	24.2	54	119.4	45.8	54.5
27	46.2	21.1	25.1	55	123.0	47.0	55.9
28	48.2	21.9	26.1	56	126.8	48.3	57.5

10. Ammonia.

Ammonia is really a gas possessing the formula NH_3; but technically it is met with almost exclusively in the form of its aqueous solution, and may be considered as having the formula NH_4OH, ammonium hydroxide. Ammonia is obtained principally as a by-product in the preparation of illuminating gas from the distillation of coal. Ammonia is very soluble in water, one volume of water at 15° C. dissolving about 730 volumes of the gas.[18] Commercial ammonia

[18] One volume of water dissolves 1050 volumes of ammonia gas at the freezing point; but the solubility rapidly decreases as the temperature rises, and at 77° F. only 536 volumes

liquor is a clear limpid liquid having a specific gravity of about 0.91, and containing about 25 percent of ammonia. The strongest solution to be met with in trade has a specific gravity of 0.88 and contains about 35 percent of ammonia. Ammonia, like soda and potash, is a strong alkali, but it does not have the same decomposing effect as the latter on animal fibers. It is used somewhat for the scouring of better class wool and for the preparation of certain emulsions of wool oils for the oiling of wool stock. It is much more expensive than either soda or potash compounds.

Analysis of Ammonia.—This is done by titration of a definite amount of the sample with 1/10-normal sulfuric acid, in the same manner as already described for the other alkalies. Each c.c. of 1/10-normal acid is equivalent to 0.0017 gm. of free ammonia, NH_3, or 0.0035 gm. of the hydrate, NH_4OH. Titration in this manner gives the free ammonia, and does not include any ammonia existing combined in the form of salts, such as sulfate, chloride, etc. To determine the combined ammonia, a definite amount of the ammonia solution is boiled in a flask with some caustic soda, and the ammonia which is liberated is passed into a definite volume of 1/10-normal sulfuric acid (or hydrochloric acid), and the excess of acid is determined by a back titration with 1/10-normal solution of sodium carbonate. The difference between the total ammonia thus found and the free ammonia as estimated above gives the ammonia existing in the combined state.

Pure ammonia water should leave no appreciable residue on evaporation to dryness. The presence of carbonates may be detected by the addition of lime water, when a white turbidity will be noticed. Chlorides may be detected by neutralizing a sample of the ammonia with nitric acid and then adding a few drops of silver nitrate, when a white precipitate or turbidity will show the presence of chlorides. Sulfates may be shown by the addition of a few drops of a solution of barium chloride, when a white precipitate or turbidity will form. The presence of lime is shown by the formation of a white turbidity on the addition of a few drops of a solution of ammonium oxalate, due to the formation of calcium oxalate.

11. Ammonium Carbonate.

The commercial salt occurs in the form of a white fibrous mass, and really consists of a mixture of ammonium bicarbonate, NH_4HCO_3, and ammonium carbamate, $NH_4NH_2CO_2$. Ammonium carbonate is also known as *sal volatile* or *salt of hartshorn*. It is made in the putrefaction of nitrogenous matter, such as stale urine, etc. It was formerly obtained by the dry distillation of bones, horn, etc., hence the name of hartshorn. At present it is manufactured by heating a mixture of ammonium sulfate and chalk. Ammonium carbonate

are dissolved. A saturated solution at 60° F. contains 58.2 percent by weight of ammonia The solution of ammonia rapidly loses strength by the volatilization of the gas if exposed to the open air, and especially if heated. One of the most characteristic tests for the presence of ammonia is its strong and peculiar odor, which has an irritating effect on the nostrils and eyes.

STRENGTH OF AMMONIA SOLUTIONS (AT 15° C.).

Specific gravity.	Percent NH_3.	Gms. per liter NH_3.	Specific gravity.	Percent NH_3.	Gms. per liter NH_3.
1.000	0.00	0.0	0.940	15.63	146.9
0.998	0.45	4.5	0.938	16.22	152.1
0.996	0.91	9.1	0.936	16.83	157.4
0.994	1.37	13.6	0.934	17.42	162.7
0.992	1.84	18.2	0.932	18.03	168.1
0.990	2.31	22.9	0.930	18.64	173.4
0.988	2.80	27.7	0.928	19.25	178.6
0.986	3.30	32.5	0.926	19.87	184.2
0.984	3.80	37.4	0.924	20.49	189.3
0.982	4.30	42.2	0.922	21.12	194.7
0.980	4.80	47.0	0.920	21.75	200.1
0.978	5.30	51.8	0.918	22.39	205.6
0.976	5.80	56.6	0.916	23.03	210.9
0.974	6.30	61.4	0.914	23.68	216.3
0.972	6.80	66.1	0.912	24.33	221.9
0.970	7.31	70.9	0.910	24.99	227.4
0.968	7.82	75.7	0.908	25.65	232.9
0.966	8.33	80.5	0.906	26.31	238.3
0.964	8.84	85.2	0.904	26.98	243.9
0.962	9.35	89.9	0.902	27.65	249.4
0.960	9.91	95.1	0.900	28.33	255.0
0.958	10.47	100.3	0.898	29.01	260.5
0.956	11.03	105.4	0.896	29.69	266.0
0.954	11.60	110.7	0.894	30.37	271.5
0.952	12.17	115.9	0.892	31.05	277.0
0.950	12.74	121.0	0.890	31.75	282.6
0.948	13.31	126.2	0.888	32.50	288.6
0.946	13.88	131.3	0.886	33.25	294.6
0.944	14.46	136.5	0.884	34.10	301.4
0.942	15.04	141.7	0.882	34.95	308.3

smells of ammonia; it is very soluble in water, and the solution forms an excellent scouring agent for wool, as it does not make the fiber harsh. It is much more expensive, however, than soda ash or even potash. The amount of ammonia salt present in a sample of ammonium carbonate may be determined in the same manner as described under ammonia, by distillation with caustic soda and collection of the evolved ammonia in a definite amount of 1/10-normal acid, then a titration with alkali to determine the excess of acid.

12. Bleachers' Assistants.

This is a general name for a class of compounds employed in the boiling-out of cotton in the kier. They are usually proprietary mixtures of varying proportions of caustic soda, soda ash and sodium silicate, and sometimes they contain soap powder. As a rule the bleacher himself could prepare these mixtures far cheaper than the manufacturer sells them, as they are frequently nothing more than a scheme for obtaining an unduly high price for an otherwise cheap alkali. Sometimes a small amount of ammonium carbonate is added

to these compounds or mixtures with the result, of course, that ammonia is evolved, and in this manner the buyer is led to believe that the preparation contains a high proportion of ammonia salts, and this serves as an excuse for charging a high price.

13. Lime.

This compound is obtained by the calcination of limestone or marble. The latter compounds are carbonate of calcium, and when strongly heated are decomposed into the oxide of calcium and carbon dioxide. The oxide of calcium is what is known as lime, and has the formula CaO. It is also called quicklime or burnt lime. It is a grayish white hard mass which combines with water with great avidity, evolving considerable heat, and crumbling to a white powdery mass. This operation is known as slaking, and quicklime so treated is termed slaked lime. The later really consists of calcium hydrate or caustic lime, and has the formula $Ca(OH)_2$. It is a strong alkali, although but sparingly soluble in water; its solution is known as lime water. Mixed with water slaked lime forms a milky liquid known as milk of lime, which is largely used in the boiling out of cotton preparatory to bleaching. It is also used in the same connection for the preparation of caustic soda solutions by mixing with sodium carbonate, calcium carbonate being precipitated.

A limestone consisting of comparatively pure calcium carbonate will yield a correspondingly pure lime which will slake well, and is known as a fat lime. If the limestone, however, contains much magnesia or silica, the lime obtained from it will not slake well, and it is called a lean lime.

Analysis of Quicklime.—(*a*) *For free lime;* 100 gms. of the sample are pulverized and completely slaked with water; the milk of lime so formed is placed in 500 c.c. flask and diluted to the mark; after shaking well, 100 c.c. of this liquid is transferred to a second 500 c.c. flask and diluted to the mark; then 25 c.c. of this liquor (equal to 1 gm. of quicklime) is titrated with normal oxalic acid, using phenolphthalein as an indicator. Each c.c. of acid used is equivalent to 0.028 gm. of quicklime, CaO. (*b*) *For carbonate of lime;* dissolve 25 c.c. of the above milk of lime in an excess of normal hydrochloric acid, which will neutralize both the free lime and the carbonate; then titrate back the excess of acid with normal alkali. The difference between the amount of acid used in this second titration and that of the first in the preceding test is equivalent to carbonate of lime; each c.c. of normal acid being equal to 0.050 gm. of $CaCO_3$.

In some bleaching establishments it is customary to prepare the caustic soda liquors employed by treating milk of lime with sodium carbonate, the lime being precipitated in the form of a mud of calcium carbonate, while the caustic soda remains in solution. In order to have a control over the proportions of lime and soda ash to employ, it is usual to analyse this lime-mud or sludge.

14. Analysis of Lime-mud.[19]

(*a*) *For Sodium Carbonate and Sodium Hydrate.*—10 gms. of the sample are mixed with ammonium carbonate and evaporated to dryness. This is for the purpose of decomposing the insoluble sodium calcium carbonate. Digest with hot water, filter, wash; dilute filtrate to 500 c.c., and titrate 25 c.c. of this solution with normal acid, each c.c. of which is equivalent to 0.031 gm. of soda, Na_2O. This soda may have been present originally either as hydrate or carbonate, the two being reported together.

(*b*) *Caustic Lime;* make up a definite portion of the lime-mud into a milk and titrate with oxalic acid as described under the analysis of quicklime. This titration will include any caustic soda present as well, and one-half of test (a) may be assumed to be this without serious error; so this is allowed for, and the remainder is calculated to lime, CaO.

(*c*) *Calcium Carbonate;* titrate with normal hydrochloric acid and Methyl Orange, and deduct from the volume the number of c.c. required in tests (a) and (b), and calculate the remainder to carbonate of lime.

STRENGTH OF MILK OF LIME LIQUORS (I).

Tw.°	Gms. per liter CaO.	Tw.°	Gms. per liter CaO
2	11.7	28	177
4	24.4	30	190
6	37.1	32	203
8	49.8	34	216
10	62.5	36	229
12	75.2	38	242
14	87.9	40	255
16	100	42	268
18	113	44	281
20	126	46	294
22	138	48	307
24	152	50	321
26	164		

STRENGTH OF MILK OF LIME LIQUORS (II).

Bé.°	CaO in 100 lbs.	CaO in 10 gallons	Bé.°	CaO in 100 lbs.	CaO in 10 gallons
10	10.6	13.3	22	16.5	24.0
12	11.6	15.2	24	17.2	25.3
14	12.7	17.0	26	17.8	26.3
16	13.7	18.9	28	18.3	27.0
18	14.7	20.7	30	18.7	27.7
20	15.7	22.4			

Lime-water is alkaline in character, although rather weak on account of the small amount of lime it contains. A gallon of clear lime-water will contain only about 1/4 ounce of lime,[20] and the strength cannot be increased by a concentration of the liquid. Lime is less soluble

[19] This is generally known by the name of "grout."
[20] A gallon of a saturated solution of lime contains 89.5 grains of calcium oxide or 118.5 grains of calcium hydroxide. One liter of water dissolves about 1.28 grams of CaO.

in hot water than in cold, one part of cold water dissolving as much as one and a half parts of boiling water.[21] The first liquor obtained from the solution of lime in water is usually more alkaline than the subsequent liquors obtained from extracting the same mass of lime. This is due to the fact that small quantities of soda and potash are present in the lime, and are dissolved in the first treatment with water.

[21] According to Herzfeld, the following table represents the number of parts of water necessary to dissolve one part of lime, CaO, at various temperatures:

°C.	Parts Water	°C.	Parts Water
15	776	50	1044
20	813	55	1098
25	848	60	1158
30	885	65	1244
35	924	70	1330
40	962	75	1410
45	1004	80	1482

Chapter XXIX.

Testing of Materials Used in Bleaching; Oils and Fats.

1. Oils and Fats.

There are a number of oils and fatty materials which find an extensive use in the scouring and bleaching of textile fabrics, or enter into related processes in connection with these operations, such as the oiling of wool for spinning and the softening of cotton after bleaching. There are also certain oils which are used directly as scouring agents, principally for the boiling-out of cotton, but also to some extent for the scouring of wool and the boiling-off of silk. These oils fall under the general class of sulfonated oils and are soluble in water. The best known representative of this group is Turkey-red oil which is prepared by the action of sulfuric acid on castor oil. Of late years similar products of a higher degree of sulfonation have been introduced on the market and have already found extensive use in the boiling-out and bleaching of cotton. Such products include Monopole Oil, Monopole Soap, Turkon Oil, Iso Soap, etc. These are in reality acid soaps and their solutions give a slightly acid reaction. As their calcium and magnesium salts are soluble in excess of the soap, these compounds are not precipitated by hard water. Monopole Oil is a more highly sulfonated product than ordinary Turkey-red oil, while Monopole Soap is prepared by separating out the sulfonated fat of castor oil from the glyceride and resulfonating and then neutralizing with alkali. The result is a solid product which has a high fatty acid content. By combining rosin soap with these sulfonated oils, such products as "Monopin" and "Leanin" are obtained; they are particularly recommended for kier-boiling.

The sulfonated oils have a high emulsifying property and even in dilute solutions and at temperatures under the boil, they readily dissolve the gums and pectin matter from cotton and other vegetable fibers, and consequently they form excellent agents for the scouring of cotton (wetting-out) previous to dyeing, and also as additions to the usual alkali in kier-boiling. In methods of cold bleaching of cotton or linen where cold solutions of sodium hypochlorite are used, it is practically necessary to use these sulfonated oil products as additions to the bleaching bath in order to obtain good results.[1]

By combining carbon tetrachloride, CCl_4, with Monopole Soap,

[1] *Ger. Pat.* 176,609.

there is obtained a product known as Tetrapole, whereas Tetrapole P is a combination of Monopole Soap and Tetrachlorethylene C_2Cl_4. The latter compound is especially recommended for kier-boiling on account of the high boiling point of the hydrocarbon. Tetraisole is a product of a similar character.

Petroleum products, benzine (naphtha) and also turpentine are sometimes added to the alkali kier-boil, with results of uncertain efficiency, however, owing to the volatile nature of the oil.

2. Benzine Soap.

Naphtha (benzine) is sometimes incorporated with soap in considerable proportion, and these so-called benzine soaps are used quite extensively in the dry cleaning industry for scouring garments and other fabrics. One method of making a benzine soap is to use an anhydrous oleate or stearate of potash, soda, or ammonia and dissolving in benzine. By using about 25 parts of the soap to 100 parts of benzine, a good firm product is obtained. One of the best known makes of benzine soap was sold under the name of Saponine (Grünewald & Stommel). According to the English patent (No. 8798 of 1895), this product was made by melting together equal parts of oleic acid and soap; heating until a clear liquid is obtained, and then allowing to cool. Soaps that are freely soluble in benzine may also be obtained by dissolving 1 part of caustic soda (or caustic potash) in 4 parts of methyl alcohol and then stirring it into the theoretical quantity (5 parts) of oleic acid (or melted stearic acid) and heating the mixture on a water bath. By increasing the proportion of the oleic acid, the solubility of the soap in benzine is increased. By dissolving 5 to 10 parts of the dry soap in benzine, a solid to semi-solid benzine soap is obtained.

3. Fats and Oils Used for Soaps for Scouring and Bleaching.

The chief natural fats which are useful for the manufacture of scouring soaps are as follows: *Tallow, palm oil, olive oil, cotton-seed oil, linseed oil, cocoanut oil,* and *palm nut oil.*

Tallow gives a very hard soap as it contains considerable stearin, the alkali salt of which has high melting point and is readily crystallized. Soaps that are very hard are generally known as *curd soaps.* They are thrown out of solution and separated from the glycerin formed simultaneously with their manufacture, by adding a saturated solution of common salt to the soap. Tallow soap is also white in color, and is usually too hard to be used by itself, as it would be liable to damage the fiber in washing and scouring, requiring a considerable amount of rubbing to produce a lather. Solutions of tallow soap cannot be made very concentrated, as on cooling they solidify. A 5 percent solution of ordinary tallow soap on cooling will give a very firm jelly. Tallow soap is also rather insoluble in water as compared, for instance, with olive oil soaps, and on this account is more difficult to remove thoroughly from the wool, especially if it has had a chance to become at all dry between the scouring and the washing baths.

Tallow is the fat obtained from sheep, cows, and other similar animals. It is a white, hard fat, and consists essentially of olein and stearin, the latter occurring in the larger amount, being about 60 percent in soft, and 80 percent hard tallows. Some tallows also contain margarin. Beef tallow contains more olein than mutton tallow, consequently is softer and better adapted for soap making; mutton tallow being used mostly for candle making. Tallow requires about 13.8 percent of caustic soda for complete saponification, and about 19.4 percent caustic potash. Pure tallow is soluble in about 40 volumes of alcohol. It generally contains a small amount of free acid, varying from 0.7 to 7 percent. When employed for soap-making this is not detrimental, but when used for lubricating purposes the presence of free acid is disadvantageous.

Tallow oil is obtained from tallow by melting the latter and preserving it in a warm room for several hours, when the stearin present will crystallize out in small granules or "seeds." This seeded tallow is pressed through cloths and the more liquid olein passes through and forms what is known as tallow oil. It is principally used as a lubricant, but some is also employed for soap making. It gives a good white soap, softer and more soluble than tallow soap.

Palm oil is a solid brownish grease which is readily saponified. It does not give as hard a curd as tallow, though its soaps are much harder than olein soaps. As palm oil on keeping rather easily decomposes to a certain extent into free fatty acid and glycerin, most samples of this oil will show a high percentage of free acid, ranging in some cases to as high as 90 percent. Palm oil is largely used in admixture with tallow for soap stock. Its soaps are of a brownish color, and possess a characteristic though not unpleasant odor. The solutions of its soaps will also solidify on cooling in the same manner as tallow soaps. Palm oil is obtained from the fruit of several species of palm trees, growing principally on the west coast of Africa. The most important tree commercially is the *Elaiis guinensis,* the fruit of which is the size of a small plum, and consists of an outer pulpy mass and a small inner kernel. The outer pulp gives the palm oil, while the kernel furnishes the palm-nut oil of trade. Palm oil consists essentially of palmitin and olein, with varying amounts of free palmitic and oleic acids. Palm oil requires about 14 percent of caustic soda for saponification, and about 20 percent of caustic potash. Palm oil may be bleached and used for the making of a white soap; the bleaching being mostly done by means of potassium bichromate. Palm oil is very seldom adulterated.

Cotton-seed oil contains more olein than the two foregoing, and consequently, it is more fluid; in fact, at ordinary temperatures it is a thin oil, resembling somewhat olive oil. It requires rather weak lye for saponification, and is difficult to salt out, as it does not yield nearly as hard a curd as tallow or palm oil. The soap ordinarily has a peculiarly disagreeable odor, which arises no doubt from the fact that cotton-seed oil is a semi-drying oil, and hence its fatty acids undergo oxidation with the production of badly smelling compounds

By improved methods of purifying the oil, cotton-seed oil soaps are now prepared of an excellent grade and quite free from any objectionable odor.

Cotton-seed oil, unless very highly purified, also contains coloring and resinous matters, which give rise to yellowish stains in the finished soap, and these may also have something to do with the bad odor of the soap. For these reasons, cotton-seed oil is seldom used by itself as a soap stock, but is always mixed with other oils. Even its soda soap is rather soft, and consequently its solutions do not solidify as readily as those of the preceding soaps. It is largely used for making soft soaps, in which connection it is employed conjointly with linseed oil.

Cotton-seed oil is obtained from the seeds of the cotton plant, *Gossypium sp.* When first obtained from the seed it is of a dark red color owing to its containig a large amount of coloring matter. This is removed by treating the oil with caustic soda, which dissolves out the coloring matter while having but little action on the oil. The refined oil has a light brownish yellow color, although it can be purified to an almost water-white oil. It contains a large amount of stearin, and consequently will congeal when cooled. In some cases, this stearin is removed by refrigeration, and is used for oleo-margarine. It also contains olein, palmitin, and a small amount of linolein. The latter gives to the oil its semi-drying quality. This oil requires about 14 percent of caustic soda or about 19.5 percent of caustic potash for saponification. It does not saponify very readily, and it is also difficult to separate the soap from the lye and obtain a perfectly neutral soap.

Olive oil is no doubt the best possible oil to be used in the manufacture of scouring soaps. The oil used for soap-making is of the third or fourth quality, the other qualities being employed for culinary purposes. The curd of olive oil is rather soft, as the oil contains a high proportion of olein, but unlike the soap of cotton-seed oil it is readily salted out. As olive oil soap is very soluble in water, its solutions remain very liquid even in highly concentrated forms.

Olive oil is obtained from the fruit of the olive tree, *Olea europaea*, the oil coming from the pulp surrounding the seed. The best grades of olive oil have a yellowish color, while the inferior qualities have a greenish brown tint. The best oils contain only about 2 percent of free acid, but when prepared from very ripe or fermented fruit the amount of acid may rise to about 25 percent. This kind of oil is called *huiles tournants,* and is used in the dyeing of Turkey-red. Olive oil requires about 13.5 percent of caustic soda, and about 19 percent of caustic potash for saponification. A very characteristic property of olive oil is that when mixed with sulfuric acid or mercury nitrate it is converted into a solid mass known as elaidin, and it possesses this property far in excess of any other oil. The best qualities of olive oil give white to cream colored soaps, while the poorer kinds give yellow to greenish soaps. True Marseilles or Castile soap is made from olive oil.

Linseed oil is a drying oil; one of its constituents being linoleic acid

which readily undergoes oxidation in the air with the formation of resin-like bodies which harden into a varnish. Hence, the use of this oil in the preparation of paints and varnishes. The soap obtained from linseed oil is very soft in character but it is not a desirable ingredient of scouring soaps on account of its drying qualities, as it is liable to dry into the fiber in the form of a varnish which it is well-nigh impossible to subsequently remove. It is only to be met with in inferior grades of soap.

Linseed oil is obtained from the seed of the flax plant, *Linum usitatissimum*. The oil is of a greenish yellow color which may vary considerably with its source. It possesses a characteristic odor and taste. It is readily saponified, and requires about 13.5 percent of caustic soda or 19 percent of caustic potash for saponification. With potash it gives a soft, clear soap of good scouring qualities, while with soda it gives a soap of the consistency of butter, so both products come under the category of soft soaps.

Cocoanut oil differs rather much in character from the previously mentioned oils in that it will not easily saponify with weak solutions of caustic alkali, but requires highly concentrated lyes. It also requires a large amount of salt for salting out, on which account its soap is employed as a hard or salt water soap, as it can be used in sea water. Soaps from cocoanut oil are also liable to become rancid in the course of time, no matter how neutral the soap may have been made, and hence it acquires a bad odor. In the better grades of soap, cocoanut oil can only be used in admixture with other oils. It is largely used, however, for cheap grades of toilet soap which are heavily loaded with water.

Cocoanut oil is obtained from the white pulp of cocoanut, the fruit of the cocoa palm, *Cocos nucifera*. The dry pulp (known as *copra*) contains about 50 percent of oil. It occurs in the form of a soft white fat, of a pleasant and characteristic odor. As it contains a considerable amount of free acid it is liable to become rancid, when its odor becomes much more pronounced. Cocoanut oil is easily saponified, on which account it is used extensively for cold process soaps. It yields a white soap with good lathering properties, and one which works well in hard or saline waters. It requires about 18 percent of caustic soda or about 26 percent of caustic potash for saponification, which is a larger amount than for almost any other fat. The chemical composition of cocoanut oil is quite complex. It consists principally of the glyceride of lauric acid, but there is also present the glycerides of caproic, caprylic, and capric acids. As these acids are all soluble in water, and as their lime salts are somewhat soluble also, and as their soaps are rather soluble in saline solutions, it is easy to understand why cocoanut oil soap works well with hard or saline waters. A small amount of stearin and palmitin are also present in cocoanut oil.

Palm-nut oil is quite similar in its properties to cocoanut oil in that it requires strong lyes for its saponification and a large amount of salt for salting out. It is chiefly used in connection with tallow, and

when thus employed is an excellent stock for the best grade of curd textile soaps.

Palm-nut oil has the consistency of butter, and is white or faintly yellow in color. It has an odor suggesting cocoanut oil. It requires about 16 percent of caustic soda or about 23 percent of caustic potash for saponification. In its chemical composition it approximates to cocoanut oil, and contains a large proportion of lower fatty acids, such as lauric, capric, caprylic, and caproic acids. The following analysis of palm-nut oil is given by Oudemans:

	Percent
Glycerides of oleic acid	26.6
Glycerides of stearic, palmitic, and myristic acids	33.0
Glycerides of lauric, capric, caprylic, and caproic aids	40.4

Palm-nut oil is not liable to become rancid, as it contains comparatively little free acid.

Besides the above mentioned fats and oils, there are, of course, a large number of miscellaneous fats used in the making of textile soaps. *Lard* is obtained from the leaf-fat of the pig. It is seldom used for soap-making, and then only for the highest grades. It is a white, soft fat, which saponifies readily giving a good hard white soap with soda and a white soft-soap with potash, both of which are readily soluble. Lard consists essentially of 60 to 65 percent of olein, and 35 to 40 percent of stearin, with small quantities of palmitin.

In the process of converting bones into fertilizer there is a by-product known as *bone-fat* which makes a fairly good soap stock if purified sufficiently; its characteristics resemble tallow. Bone-fat is used for the preparation of cheap grades of soap. It is a grayish, granular fat of a somewhat softer consistency than tallow. It is liable to become rancid owing to the presence of animal tissue. It also contains, as a rule, a rather large amount of free acid, ranging from 7 to 12 percent. As it always contains a small quantity of calcium phosphate, this serves as a characteristic test for bone-fat. It is also liable to contain considerable water. Gray mottled soaps are usually made from bone-fat.

A few of the less important oils for soap-making are the following:

Castor oil, obtained from the seed of the castor oil plant, *Ricinus communis.* The seeds contain about 50 percent of oil, which is obtained by pressing. It is distinguished from other oils by its high viscosity, and its ready solubility in alcohol. The oil consists principally of the glyceride of ricinoleic acid together with a little palmitin, so it differs very radically from other oils in its composition. Ricinoleic acid appears to be a hydroxyacid and is therefore capable of readily forming esters with sulfuric acid; and, in fact, these bodies are used largely for the preparation of Turkey-red oils. Castor oil is easily saponified and gives a very soluble soap with soda, which is also clear and transparent. The oil requires about 12.5 percent of caustic soda or about 17.5 percent of caustic potash for saponification, which is rather less than most of the oils and fats. Castor oil is liable to become rancid on keeping.

Corn oil is a by-product in the manufacture of starch and glucose from corn or maize. It is amber-yellow in color and possesses an odor and taste resembling corn. It is easily saponified, requiring about 13 percent of caustic soda or 19 percent of caustic potash for saponification. The soap is of a yellowish color and resembles cotton-seed oil soap in its properties and qualities.

Rape-seed oil is obtained from various species of rape plants, *Brassicae sp.* The oil is brownish green to yellowish green in color, and has a characteristic odor. It only requires 12.5 percent of caustic soda or 17 percent of caustic potash for saponification. It gives a greenish yellow soap having a strong odor, and, furthermore, the soaps are very soft, even the soda soap being pasty in consistence. Rape-seed oil consists principally of the glycerides of brassic, rapic, and brucic acids. Like linseed oil it is a drying oil.

Whale oil, also known as *train oil,* was once largely used for soap-making, but at present it is seldom employed for this purpose. It is obtained from the blubber of whales, and is a dark reddish colored oil with a fishy odor and taste. It requires about 13.5 percent of caustic soda or about 19 percent of caustic potash for saponification. The soaps are of a brownish red color and have a fishy odor; they are very soft, even the soda soap being of butter-like consistency. Whale oil is characterized by containing a considerable amount of valeric acid, a volatile acid of the stearic series.

4. Wool Oils.

By wool oils are understood such oils or emulsions [2] added to the wool stock before carding or spinning for the purpose of lubricating the fibers, and enhancing the spinning qualities of the same. A discussion concerning the necessary qualifications for a good wool oil has already been taken up in a previous section of this book. As considerable information may be deduced from the element of cost of a wool oil as to its probable composition, it may be said that the cheapest oils employed for this purpose are the heavier grades of mineral or hydrocarbon oils obtained from petroleum and shale, and rosin oils; next in regard to cost are the so-called oleins obtained in the distillation of recovered grease from wool scouring; this class is largely used and are very serviceable for most purposes. Next in grade comes oleic acid obtained as a by-product in the manufacture of candles and glycerin; it occurs in various degrees of purity, and, as a rule, makes a very good wool oil. The highest class, and most expensive as to cost, are the various animal and vegetable oils, such as lard oil, tallow oil, olive oil, cotton-seed oil, etc. Olive oil in particular forms the typical wool oil.[3] One of the first considerations in a wool oil is the

[2] Emulsions are largely employed for wool oils; they are generally prepared from neutral oils, oleic acid, etc., with aqueous ammonia, solutions of soda ash or borax, or a soap solution. Sometimes, in order to produce a more perfect emulsion, gum or gelatine-like substances are added. These may be detected in such an emulsion by adding strong alcohol, which will cause the precipitation of these substances.

[3] Hurst recommends that where the price is a principal consideration, the best oil to employ for the oiling of wool stock, and one with which the risk of spontaneous combustion is reduced to zero while the firing risk is also slight, would be a mixture of 80 percent of good olive, lard, neatsfoot, or peanut oil with 20 percent of mineral oil with a flash point of 420° F.

readiness with which it is emulsified by alkalies and soap solutions; the mineral and rosin oils are not saponifiable and are rather difficult to emulsify;[4] the oleins also contain products which are not saponifiable, and if the amount is excessive, it will retard the scouring action of the soap liquors employed for washing the wool; oleic acid and the animal and vegetable oils are easily saponified and emulsified, hence are easy of removal. In many cases wool oils are made by blending together various oils, and thus fatty oils, oleins and mineral oils may be found together. Another important consideration in the selection of wool oils is the question of the spontaneous inflammability of the oiled wool, as in many cases wool or cotton oiled with certain oils and exposed to the air will gradually heat up, and finally reach a sufficient temperature to ignite and cause serious fires.[5] Certain oils possess the property of absorbing oxygen from the air with considerable rapidity, and in doing so undergo chemical reactions which cause the development of considerable heat; such oils are known as drying oils, because as a result of their oxidation they yield dry and hard films like varnish. This class includes linseed and poppyseed oils as the chief representatives. A second class of oils also absorb oxygen, but only slowly and to a limited amount, and yield only thick viscous films which do not completely dry or harden; this class is known as semi-drying oils, and includes cotton-seed oil as its chief representative. The third class of oils do not appear to suffer oxidation at all, or only to a very slight degree, and are termed non-drying oils; this class includes olive oil, lard oil, etc.[6] The hydrocarbon oils do not absorb oxygen at all, and consequently cannot cause spontaneous combustion, and it has even been shown that the mixture of mineral oils with fatty oils prevents the latter from causing wool or cotton to take fire.[7]

(*a*) *Determination of Degree of Spontaneous Combustibility.*[8]—This is best estimated by the use of an apparatus devised by Mackay,

[4] Mórawski states that as much as 80 parts of mineral oil yields a complete emulsion with 10 parts of oleic acid and 10 parts of a half percent soda solution

[5] The fire insurance companies in England give the following schedules for wool oils: (a) free from any extra charge are olive oil (Gallipoli), lard oil, olein not containing more than 10 percent of unsaponifiable matter, fish oil or a manufactured oil not containing more than 30 percent of unsaponifiable matter, and having a flash point of not under 340° F.; (b) a higher rate is charged for manufactured oils containing more than 30 percent, but not more than 50 percent of unsaponifiable matter; (c) a still higher rate is charged for black (recovered) oil containing not more than 50 percent of unsaponifiable matter; (d) the highest rate is charged for manufactured oils containing more than 50 percent of unsaponifiable matter, or mineral oil, oil of pine, linseed oil, rape oil, cotton seed oil, or any other seed oil

[6] Fox (*Oil & Colorman's Jour.*, 1884, p. 234) has shown that linseed oil will absorb 191 c.c. of oxygen for each gram of oil, while olive oil will only absorb 8.2 c.c., and cotton-seed oil 24.6 c.c.

[7] Galletly obtained the following results by saturating a handful of cotton-waste with various oils, wringing out the superfluous oil, and then placing the oily waste in a chamber kept at a temperature of about 150° F., at which oxidation begins:

Boiled linseed oil—one sample fired in 75 minutes, another in 105 minutes.
Raw linseed oil—two samples fired in 4 and 5 hours respectively.
Rape oil—sample over night was completely consumed, including box and waste.
Olive oil—two samples fired in 5 and 6 hours respectively.
Lard oil—fired in 100 minutes.
Sperm oil—did not ignite or char the waste.
Mineral oils—refused to ignite, and mixtures of 80 parts rape oil and 20 parts mineral oil and of 50 parts seal and 50 parts of mineral oil did not develop a temperature sufficient to char the cotton.

[8] The production of spontaneous combustion in oiled wool or other fibers, is governed by several factors, and the exact conditions of its development are not thoroughly known. The nature of the oils employed, of course, has perhaps first place in the consideration; the

the construction of which can be seen in Figure 299. To carry out the test, 7 gms. of bleached loose cotton are soaked with 14 gms. of the oil under examination and placed in the inner cylinder. The water in the surrounding water-bath is brought to the boil, the thermome-

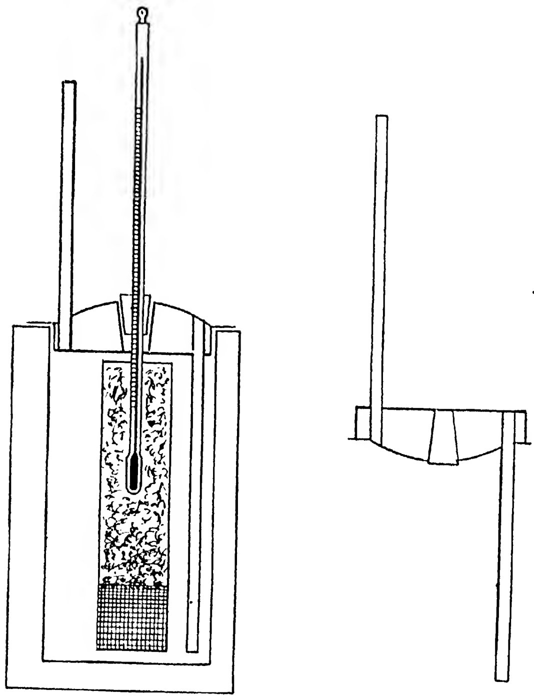

Fig. 299.—Mackay Apparatus for Testing Spontaneous Combustion of Oiled Stock.

ter is immersed in the cotton, and after one hour the temperature is read. The boiling is continued until the thermometer no longer shows any rise in temperature, and the time for this maximum is also taken An oil which reaches the maximum temperature of over 200° C before the expiration of two hours should be regarded as dangerous; and in fact any oil which reaches a temperature of 100° C. before the expiration of one hour may be regarded as dangerous. From the results of experiments it was found that fatty acids are more liable

proportion of the oil to the material has also considerable bearing on the question; also the volume of the oiled material for the greater the surface exposed to the oxidizing action of the air, the greater the liability to combustion; the presence of moisture has considerable influence, for it has been found that the presence of a small amount of moisture tends to promote spontaneous combustion rather than retard it; probably the moisture acts as a carrier of oxygen to the oil, or else the high specific heat of the water enables it to accumulate much heat, and so raise the general temperature of the mass. The temperature of the place where the oiled material is kept also exerts an influence, for the oxidation of the oils and the heating of the material is more likely to occur where the temperature is high than where it is low.

to cause spontaneous combustion than the neutral oils, while the addition of a mineral oil lessens the tendency to spontaneous combustion.[9]

Professor Ordway has also investigated the subject of the spontaneous combustion of oils, and has devised an apparatus as follows: The outer shell consists of a 6 in. wrought iron tube, which can be closed at each end by wooden disks. Inserted within this tube is an inner 4 in. tube of sheet iron, with overlapping metal covers at the end. There is thus left an air-space of one inch around the inner tube and one of three inches at each end. The apparatus is placed on a tripod stand and heated with a Bunsen burner. In carrying out the test, 50 gms. of the oil are evenly distributed over 50 gms. of cotton-waste, and then carefully pushed into one end of the inner tube, and the bulb of a thermometer inserted into the ball thus made. A second ball of unoiled waste is placed at the other end of the tube, and a thermometer also placed within it. A third thermometer is inserted so that the bulb is in the middle of the inner tube between the two balls of waste. On heating the apparatus, the reading on the second thermometer in the oil waste should not rise above 100 to 101° C., while the third thermometer should be kept at about 120° C.[10]

(*b*) *Flash-point.*—Place about 50 c.c. of the oil in a small porcelain dish and heat on a sand bath over a Bunsen burner; constantly stir the oil with a thermometer, and from time to time bring a small

[9] Mackay gives the following results of his experiments on various oils:

Oil used	Temp in 1 hr °C.	Temp. in 1½ hrs °C	Maximum Temp. °C	Maximum Temp. Time
Cotton-seed oil pure .	125	...	242	1 hr. 15 m.
Cotton-seed oil pure	121	282	284	1 35
Olive oil fatty acids .	105	...	293	1 55
Olive oil fatty acids	114	...	196	1 25
White Australian olein	103	191	230	1 45
Olive oil	98	104	241	3 25
Olein	98	102	110	2 08
Belgian olein ..	98	100	173	3 16
Olive oil neutral ...	98	101	235	5 15

[10] Bishop (*Jour. Pharm.*, 1896, 55) gives the following method for the determination of the oxidizability of an oil: As the oxidation of the oil is greatly facilitated by the addition of a little manganese resinate (which is obtained from the commercial product by extraction with petroleum ether), 5 to 10 grams of the sample of oil are mixed 2 percent of the resinate until the latter is completely dissolved. The solution (1 2 grams) is intimately mixed with 1 gm of calcined pure silica and exposed to the air at a temperature of 17 to 28° C.; in the case of non drying oils, such as colza and olive oils, the best temperature is 20 to 30° C. Weighings of the sample are taken at the end of 2, 6, and 16 hours, and a fresh surface is exposed after each weighing. The following numbers give the maximum percentage increase of weight given by the respective oils:

Oil	Density	Percentage Increase
Linseed (French)	0.9327	17.05
Linseed (La Plata)	0.9304	15.20
Hemp-seed	0.9287	14.40
Poppy-seed	0.924	14.20
Nut Oil	0.924	13.70
Cotton-seed (demargarified)	0.923	9.45
Cotton-seed	0.924	8.60
Sesame (Senegal)	0.9215	8.70
Sesame (Indian)	0.921	7.40
Palm	0.916	6.70
Palm (White)	0.916	6.50
Colza (French)	0.9142	6.40
Colza (Indian)	0.9137	5.85
Olive	0.9155	5.30

flame towards the surface of the oil. That temperature is noted as the flash-point when there is a slight explosion or flash. The rise in temperature in heating the oil should not be more than 10° F. per minute. The flame for causing the flash may be very conveniently obtained by connecting an ordinary mouth blowpipe with the gas supply, and so regulating the flame at the jet that it is about the size of a small pea. In the progress of this test, besides noting the flash-point, there may also be noted the vaporizing-point and the burning-point. The vaporizing-point is the first to be observed, and it is that temperature at which the vapor of the oil begins to be observed; it is also known as the smoke-point. It is not considered of much importance as far as determining the fire risks of the oil; though oils with a low vaporizing-point (say of 150 to 160° F.) would be unpleasant to work with. The flash-point is the next to be noted, and is taken as above described. In making the test care should be had not to allow the flame to touch the surface of the oil. The higher the flash-point the safer will be the oil, as this marks the point at which an inflammable vapor is given off; 350° F. is considered quite a safe point, and there is no necessity to much exceed this, as far as wool oils are concerned. After the flash-point has been noted, if the heating of the oil is continued, it will be found that the flashing becomes more continuous, and after a while, the flame instead of going out, will continue to burn. The temperature at which this occurs is the burning-point, or *fire-test* of the oil. In America this point is considered of much importance, as it has a very intimate relation to the liability of the oil to spontaneous combustion.

(*c*) *Determination of Amount of Mineral Oil.*—This determination is based on the fact that whereas the vegetable and animal oils are readily saponified by strong solutions of caustic alkalies, the mineral oils are not. To detect the presence of mineral oil in a mixture, a piece of caustic potash about the size of a pea is dissolved in 5 c.c. of alcohol, and then a few drops of the sample to be tested are added, and the mixture boiled for several minutes, after which 3 to 4 c.c. of distilled water are added. If the solution remains clear only fatty oil is present, but if the solution becomes turbid, mineral oil is present. A quantity as small as 2 percent of the latter may be shown by this test. The amount of the mineral oil present may be estimated as follows: 25 gms. of the oil are mixed with 10 to 15 c.c. of a caustic potash solution (68° Tw.), 25 c.c. of water, and 5 c.c. of alcohol: the mixture is boiled with constant stirring for one hour, by which time the fatty oils will be saponified. The mixture is then placed in a separatory funnel, some warm water and 25 c.c. of petroleum ether added. The whole is shaken for several minutes, then allowed to stand, when it separates into two layers; the upper layer consists of the petroleum ether containing the mineral oil in solution, while the lower or aqueous layer contains the saponified fatty oil. The latter is run off, water is added, the mixture shaken up and again allowed to stand, after which the lower aqueous layer is again run off. This washing is repeated until the aqueous layer is clear. The ethereal so

lution is then poured into a weighed glass and evaporated on a water-bath, and finally the residual oil is weighed.[11]

(*d*) *Saponification Test.*—This is a rather important test, as it may lead to some idea as to the probable composition of the oil. It refers to the percentage of the oil which may be saponified by alkalies, and is carried out as follows: 2 gms. of the oil are weighed in a flask, and 25 c.c. of a N/2 solution of alcoholic potash are added; the flask is fitted to an inverted condenser, and heated on a water-bath until the oil is thoroughly saponified. To hasten the action, the flask is shaken from time to time. After the saponification is complete, the flask is removed and the contents are allowed to cool. A small quantity of phenolphthalein solution is then added, and the liquid is titrated with a N/2 solution of sulfuric acid, until the red color of the indicator disappears. A blank test on the potash solution is now made by boiling 25 c.c. in the flask for half an hour, and then titrating the contents with the acid as before. The difference between the two amounts of acid used gives the quantity of potash required to saponify the oil. This quantity multiplied by the factor 0.028 gives the amount of caustic potash, KOH, in grams, and this multiplied by 100 and divided by the weight of the oil, gives the weight of caustic potash required to saponify 100 parts of the oil.

Horwitz gives the following method for analyzing oil emulsions for wool: Two grams of the material are weighed in a flask and extracted for a couple of hours with frequent shaking with ether-alcohol mixture. Any sodium carbonate present will remain undissolved, and is collected on a tared filter, and dried and weighed. The filtrate is divided into two parts, one of which is evaporated to dryness, giving the fat, while to the other portion hydrochloric acid is added in excess, and the ammonia present is precipitated with platinic chloride; the ammonium-platinic chloride is filtered off, dried, ignited and weighed as platinum, from which the amount of ammonia may be calculated. The water is calculated by difference, or determined by drying a portion of the emulsion at 120° C. and subtracting the ammonia found.[12]

Oils that resemble olive oil require, as a rule, from 19 to 19.5 percent of potash, rape oils from 17 to 17.6 percent, drying oils from 18.5

[11] Birl (*Archiv. der Pharm*, vol. 225, p. 310) gives the following method for determining mineral oil in a vegetable oil (more especially in olive oil): Dissolve 65 grams of caustic potash in one liter of 95 percent alcohol, and the solution is made of such a strength that 10 c.c. are neutralized with 10 c.c. of normal sulfuric acid; 10 grams of the oil to be examined are boiled for 10 minutes in a porcelain dish with 40 c.c. of the potash solution; water is then added until the volume is 100 c.c. The mixture is again warmed with shaking, whereon the soap formed goes into solution, and then titrated with normal acid using phenolphthalein as the indicator. Pure oils require 6 c.c. of acid (with the exception of castor oil and the oils from the *cruciferæ*, which require from 7 to 8 c.c.); vegetable oil with 10 percent of mineral oil requires 8 c.c.; with 20 percent of mineral oil 11 c.c. of acid.

[12] The amount of water and dirt present in wool oils is a factor in their analysis which should not be overlooked. They may be determined in the following manner: 20 gms. of the well-mixed sample are dissolved in about 100 c.c. of petroleum ether, and the solution is then allowed to stand for one hour, after which it is filtered through a weighed filter, taking care to allow no drops of water to pass on to the filter with the petroleum ether. Both the filter and the flask in which the oil was dissolved are washed several times with the petroleum ether, and then carefully freed from the solvent by evaporation, and weighed; the water is afterwards driven off from the flask and its quantity and the amount of the dirt determined by reweighing. (Honig and Spitz, *Zeit. f. angew. Chem.*, 1891, p. 565.)

to 19 percent, whale oils 18.75 percent, solid fats like tallow 19.25 to 19.8 percent, butter 24 percent, and sperm oils from 12.3 to 14 percent. If the oil contains any large amount of mineral oil, this would be shown by an abnormally low saponification test, and it is possible to calculate the approximate amount of such adulteration by multiplying the percentage of caustic potash obtained by 100 and dividing by 19, which would give the percentage of fatty oil present, and the difference between 100 and this figure would give the approximate percentage of mineral oil.

A good wool oil should contain a minimum amount of free acid; in general there will hardly ever be found any appreciable quantity of mineral acid present,[13] and this is only liable to occur in low-grade oils where sulfuric acid has been used in the processes of recovery and has been completely removed.[14] The presence of free acid in a wool oil is especially objectionable on account of its corroding action on the cards which also results in a considerable amount of iron being deposited in the fiber. This is afterwards difficult to remove by the usual methods of scouring and gives rise to many faults in dyeing. Certain oils [15] are especially liable to contain free fatty acids, and these should be avoided in the preparation of wool oils.

(*e*) *Estimation of Free Fatty Acid in Wool Oils.*—Most of the olive oils from southern Europe contain as little as 5 percent of free oleic acid. These may be used for the finest classes of wool with safety. Even oils containing up to 8 or 9 percent of free fatty acid give good results, but above that there is danger of clogginess; the acid also has a bad effect on the pins of combs and fallers thus costing

[13] Mineral acids are only accidentally present in fixed oils, and usually exist in very small proportions Mineral acids may be easily recognized by agitating the oil with warm water, separating the aqueous layer, and testing it with a solution of Methyl Orange, which will give an orange or red coloration if any mineral acid be present. The nature of the mineral acid, which is most commonly sulfuric, can then be ascertained by testing the aqueous liquid with barium chloride, which will give a white precipitate in the presence of sulfuric acid; with silver nitrate, which will give a white precipitate if hydrochloric acid is present. (Allen, *Comm. Org Anal*, vol II, part I, p 140)

[14] Animal fats when freshly prepared, contain but infinitesimal quantities of free fatty acids, and may, therefore, for practical purposes, be considered as consisting of absolutely neutral glycerides Fats of vegetable origin, however, mostly contain notable amounts of free fatty acids Experiments by Rechenberg (*Berichte*, 1881, 2217) have shown that unripe seeds contain considerably larger quantities of free acids than ripe ones. The amount of free fatty acids in vegetable fats increases on keeping, this is especially noticeable in the case of palm oil, which gradually decomposes on standing for some time into free fatty acids and glycerin. Fresh cotton-seed oil is completely free from fatty acids, owing to its being refined by means of caustic alkalies (Lewkowitsch, *Oils, Fats and Waxes*, p 50)

[15] Nordlinger (*Jour. Soc Chem. Ind*, 1889, p 685) gives the following table for the amount of free fatty acids in various vegetable oils, the percentages being calculated on a basis of oleic acid.

Oils and Fats	Percent of Free Fatty Acids		
	Min	Max	Mean.
Rape	0 52	6.26	2.88
Olive	3 87	27.16	12.97
Poppy-seed	12 87	17.73	15.37
Arachis	3 58	10 61	6.52
Sesame	7 17	33 13	17.94
Cotton seed	0 42	0 50	0.46
Castor	0 62	18.61	9.28
Linseed	0 41	4.19	1.57
Candlenut	....	....	56.45
Palm-nut	3 30	17.65	6.91
Palm (old sample)	....	....	50.82
Cocoanut	3.03	14.35	7.92
Mowrah seed	....	....	28.54

The oils described in the above table are commercial grades; salad and extracted oils, as a rule, show a much smaller amount of free fatty acids.

more in the end than the difference between a good and bad oil. Oils showing over 8 percent of free fatty acid should be rejected for worsted tops, but even these can be used on lower grades of wool stock. Free fatty acids have an acid reaction in alcoholic solution, while neutral fats have not.[16] Therefore the free acid may be estimated in the following manner: About 50 gms. of the oil are placed in a stoppered flask together with 100 c.c. of neutral methylated alcohol containing a little phenolphthalein and the liquid is raised to the boiling point by immersing the flask in hot water. The contents of the flask are well shaken in order that the solution of the fatty acids may be as complete as possible. If the oil be entirely free from acid, the pink color of the liquid will remain unchanged, but if free acid is present it will have disappeared. If the latter is the case, the liquid is titrated with a N/2 solution of caustic soda. The latter should be added in small amounts to the warm contents of the flask with thorough agitation after each addition until the pink coloration persists after vigorous shaking. Each c.c. of N/2 caustic alkali corresponds to 0.128 gm. of palmitic acid, or to 0.142 gm. of stearic acid, or to 0.141 gm. of oleic acid. When only a small amount of free acid is present it is best to use a N/10 solution of alkali. The presence of soap and hydrocarbon oils does not interfere with this reaction.[17]

5. Testing of Olive Oil.

As this oil is extensively used as a wool oil, and as it also is subject to considerable adulteration, especially with cotton-seed oil, it will not be going beyond the province of this subject to give a few tests for its purity. To determine if a sample of olive oil is adulterated with cotton-seed oil, a portion of the oil is shaken with an equal measure of nitric acid of specific gravity 1.37, when a coffee-brown coloration is produced if cotton-seed oil is present. This test will indicate with ease the presence of as low as 2 to 3 percent of cotton-seed oil, especially if the test is made side by side with a sample of pure olive oil for comparison. The presence of rape-seed oil in olive oil with the same test will give a yellowish brown color. Another test known as Becchi's test for cotton-seed oil is as follows: Two reagents are prepared, (I) 1 gm. silver nitrate, 200 c.c. alcohol, 40 c.c. ether, 0.1 gm. nitric acid; and (II) 100 c.c. amyl alcohol with 15 c.c. colza oil. To carry out the test, 10 c.c. of the oil under examination are mixed in a test-tube with 1 c.c. of reagent I, and then shaken with 10 c.c. of reagent II. The mixture is divided into two equal portions, one of which is put aside for future comparison, while the other is immersed in boiling water for about 15 minutes. The heated sample

[16] Free fatty acid in an oil may be detected by shaking the sample with alcohol, and adding an alcoholic solution of lead acetate to the liquid. If any notable quantity of free fatty acid is present, a white precipitate will result. Rosin and soap, however, produce the same reaction, hence this test is not applicable in the presence of these latter bodies. (Allen, *Comm. Org. Anal*, vol. II, part I, p. 140.)

[17] If resin acids, however, are present in the sample, they will also be estimated by the above process as fatty acids. If resin acids are present, they may be separated from the free fatty acids by a variety of methods. One method depends on the solubility of the barium salts of the resin acid in alcohol. Gladding's method of separation depends on the ready solubility of silver resinate in ether, whereas the silver salts of the fatty acids are insoluble in that reagent.

is then removed and its color compared with that of the other sample. The presence of cotton-seed oil is indicated by a reddish brown coloration in the heated sample.[18]

Horwitz recommends the following test to detect the presence of a drying oil in olive oil: A well-cleaned copper wire is placed in a mixture of 2 c.c. of nitric acid and 5 c.c. of the oil; the mixture is then stirred with a glass rod, and the wire is withdrawn after a half hour. In the presence of a drying oil, the wire will have a pink shade.

The following tests have been recommended for the detection of adulterations in olive oil: (a) for linseed oil; add 2 c.c. of nitric acid to 5 c.c. of the sample, and introduce a piece of bright copper wire into the mixture; if the wire acquires a rose color after half an hour linseed oil is present. (b) For cotton-seed oil, mix a sample of the oil with an equal volume of concentrated nitric acid, when a brown color indicates the presence of cotton-seed oil. (c) For sesame oil, to a sample of the oil add an equal quantity of concentrated hydrochloric acid and a fragment of cane sugar; if after shaking and standing, a red color is developed, sesame oil is present.[19] (d) For colza oil, saponify 10 gms. of the oil with an alcoholic solution of caustic potash, when a darkening of the color will show that colza oil is present. (e) For peanut oil, the oil is saponified with alcoholic potash solution, and the separated soap is warmed to free it from alcohol; it is then decomposed with hydrochloric acid, and the liberated fatty acids are dissolved in boiling alcohol; the separation of arachidic acid, which is recognized by its mother-of-pearl luster, will indicate the presence of peanut oil.[20]

[18] Brullé (*Compt rend* vol 112, p 105) extends this test to the detection of other impurities in olive oil He uses a solution containing 25 parts of silver nitrate dissolved in 1000 parts of 95 percent alcohol; 5 c.c. of this solution being added to about 12 c.c. of the oil under examination which should be filtered if not quite clear. The test tube containing the mixture is then heated in boiling water and the effect observed. The following table of reactions is given:

Kind of Oil	Color Reaction
Virgin olive oil	Bright green
Olive oil of 2nd and 3rd pressures, containing some olive-kernel oil	Darkens slightly, quickly changing to intense green
Olive oil of inferior quality, strongly colored	Same as previous oil, but takes longer. (15 to 29 mins)
Cotton-seed oil, pure.	Black.
Peanut oil.	Brownish red, greenish as it loses transparency
Sesame oil	Dark reddish brown, not changing to green.
Rape-seed oil	Greenish yellow, then opaque
Poppy-seed oil.	Same as preceding.

Brullé states that it is possible with practice, to determine in many cases, thus colorimetrically, 5 to 10 percent of one of these oils in a mixture. We believe, however, that such a method of analysis would have its accuracy based on the intuition of long experience rather than on the definiteness of the reactions themselves.

[19] Lalande and Tambon (*Jour. Pharm. Chim.*, vol 23, p. 234) consider this test as unreliable, and propose the following: 15 c.c. of the oil are shaken up in a test-tube for a couple of minutes with 5 c.c. of colorless nitric acid of sp. gr 1 4; a yellow coloration of the acid on settling indicates the presence of sesame oil. Olive oil, peanut oil, and cotton-seed oil leave the acid colorless.

[20] Renard's method (*Zeit. f. Anal. Chem.*, 1873, p. 23) for the determination of peanut oil in olive oil is as follows: 10 gms. of the oil are saponified, the fatty acids are precipitated by the addition of hydrochloric acid and dissolved in 90 percent alcohol. From this solution the lead salts are precipitated by the addition of lead acetate. The precipitate is extracted with ether, which dissolves the oleate, and leaves a residue consisting mainly of lead palmitate

The following test for the purity of olive oil has been proposed by Audoynaud:[21] 2 c.c. of the sample are placed in a test-tube with 0.1 gm. of powdered potassium bichromate and shaken for several minutes; then a mixture of nitric and sulfuric acids is added until the total volume is about 4 c.c., when it is again shaken, whereby the oil becomes a reddish brown. After standing for 2 minutes, the volume is brought to 5 c.c. by the addition of ether, and then again shaken. After a few minutes a violent effervescence takes place, nitrous fumes are evolved, and the oil rises to the surface with a characteristic coloration. Pure olive oil will have a green color, but if the oil contains at least 5 percent of sesame oil, arachnis oil, cotton-seed oil, or poppy-seed oil, the coloration will be yellowish green to yellow or even orange.[22] In order to better observe these colors water is added, and the color is permanent for some hours.

Milliau[23] proposes the following methods for the testing of the purity of olive oil. The detection of cotton-seed oil is based on the reducing power of the fatty acids of this oil, a property entirely wanting in the fatty acids of olive oil. In a porcelain basin of about one liter capacity, 15 c.c. of the oil to be examined are heated to 110° C. At the same time 15 c.c. of an aqueous solution of caustic soda of 76° Tw. are slowly added and 15 c.c. of 95 percent alcohol. When the mass on boiling becomes homogeneous, a sign that the saponification is complete, about 500 c.c. of distilled water are gradually added so as not to lower the temperature of the paste, nor to make it thick. After boiling for a few minutes the fatty acids are separated by the addition of a 10 percent solution of sulfuric acid. When the separation is complete and the sulfuric acid is in slight excess, 5 c.c. of the fatty acids are removed with a silver spoon to a test-tube; 20 c.c. of 95 per cent alcohol are added, and the tube is heated on a water-bath until the fatty acids are dissolved, then 2 c.c. of a solution of silver nitrate (30 gms. of the salt per 100 c.c.) are added, and the tube is heated on a water-bath till about one-third of the contents have evaporated. If the olive oil is pure, the fatty acids remain unchanged; if, however, cotton-seed oil be present, no matter what proportion, the silver reduced to the metallic state blackens the fatty acids. This reaction is very delicate.[24]

and arachidate These are decomposed with hydrochloric acid, and the fatty acids are dissolved in 50 c.c. of warm 90 percent alcohol, and carefully crystallized. The arachidic acid which separates out is filtered off and washed with 70 percent alcohol It is then dissolved off the filter with hot alcohol, and brought into a tared filter from which the alcohol is evaporated, and the acid may then be weighed Note should be taken of the amount of the acid dissolved by the alcohol used in washing.

[21] *Compt. rend.*, vol. 101, p. 752

[22] With respect to the adulteration of olive oil with other vegetable oils, Peters (*Arch. Pharm.*, 1888, 322) makes the following observations: (a) The melting point of the mixture of insoluble fatty acids obtained by saponification of the oil with hydrochloric or dilute sulfuric acid is determined; in pure olive oil this should be between 24° and 29° C; if above 29° C cotton-seed oil is present; if below 24° C. linseed, poppy, or castor oil is present. (b) The different solubilities of the fatty acids in 90 percent alcohol; such a solution of the fatty acids from cotton-seed or peanut oil solidifies at 15° C, so that if these oils be present in olive oil, the alcoholic solution of the fatty acids will become turbid at 15° C.

[23] *Monit. Scient.*, 1888, p. 366.

[24] The following tests with sulfuric acid are useful for detecting adulterations in olive oil used for a wool oil:

(1) Place 10 drops of the oil to be tested in a colorless glass vessel and in the center drop a small drop of sulfuric acid. If the oil is pure it will assume a pale yellow ap-

The presence of iron may be detected in olive (or other oils) in the following manner: About 10 c.c. of the oil are shaken up in a test-tube with an equal quantity of water acidified with sulfuric acid and containing a few drops of a solution of potassium ferrocyanide. A few c.c. of ether are then added and the mixture shaken up again The oil dissolves in the ether and floats on the surface of the water; if iron is present a layer of Prussian Blue forms at the border line between the two liquids. By comparing the depth of color with similar tests on the same amounts of liquids containing definite amounts of iron a quantitative estimation of the amount of the latter in the sample may be obtained.

6. Testing of Olein.

Olein is rather extensively employed in the preparation of wool oils; it is generally valued by determining its percentage of fatty acids. This may be done in the following manner: Heat 10 gms. of the sample with 25 gms. of white wax and 75 c.c. of a cold saturated solution of common salt, in which the liberated fatty acids are practically insoluble. When cold the resultant cake should be dried between filtered paper, and then gently heated until all trace of water is removed, and then weighed.

pearance which gradually changes to a yellowish green. If poppy oil is present a deep yellow color will be formed which at length becomes almost opaque.

(2) By the same test rape oil produces a ring of greenish blue around the drop of acid, with some light yellow brown streaks in the center.

(3) If linseed oil is present it becomes almost black.

(4) Whale oil, when the acid is dropped in, produces a movement in the center gradually extending and at length shows a red tint with violet edges

(5) If lard or tallow is present the liquid acquires a decided brown shade.

(6) To detect the presence of cotton-seed oil, pour some clean water into a shallow vessel, and then let one drop of the oil to be tested fall into it. Pure olive oil will at once break into fragments. A sheet of white paper is gently laid on the surface of the liquid, and if held up to the light will show a rose-shaped webby figure. If cotton-seed oil is present the figure will be blurred.

Chapter XXX.

Testing of Materials Used in Bleaching; Soaps.

1. Soaps.

Soaps are compounds prepared by treating an oil or fat with an alkali. Chemically considered, they consist of the alkali salts of certain fatty acids. The alkalies which may be employed for soap-making are caustic soda and caustic potash; the former yields soaps which give a curd capable of being crystallized, and hence are *hard*, while the latter gives soaps of a pasty character, which are not crystalline in structure and are called *soft* soaps. Ammonia might be used as the alkali for soap-making, but the ammonium soap formed is not very stable as the alkali is of a volatile nature, and hence the soap is liable to gradual decomposition with the liberation of ammonia and the formation of free fatty acid; ammonia soaps would also be too expensive for general purposes. The compounds of the fatty acids with other bases such as lime, alumina, etc., are insoluble in water, and hence cannot be used as soaps.

The fats and oils which may be used in the making of soaps are numerous and varied. The only real difference between an oil and a fat is one of melting point, the oils being liquid at ordinary temperatures, whereas the fats are solid or pasty. Oils and fats, both of animal and vegetable origin, consist chemically of compounds of glycerin with various fatty acids. Glycerin is a tri-basic alcohol and acts towards an acid in the manner of a mild base. The fatty acids are analogous to acetic acid, only of higher molecular weight: they are greasy insoluble substances of a mildly acid character. The fatty acids which occur in greatest amount in the oils and fats are palmitic, stearic, and oleic acids. The glycerides, or compounds of glycerin with these acids, are known respectively as palmitin, stearin, and olein. As glycerin is a tri-basic alcohol, the glyceride consists of a combination between three molecules of glycerin with one molecule of fatty acid. Nearly all of the fats and oils contain the three glycerides in varying proportions; and it is this difference in the relative amounts of the three glycerides present that causes differences in the character of the fats and oils. For instance, in olive oil, olein predominates; in tallow, stearin predominates; and in palm oil, palmitin predominates. Besides these three glycerides mentioned, each oil or fat also has small amounts of other glycerides of various fatty acids, which give the characteristic taste, odor, etc., to the particular fat or oil.

When a caustic alkali acts on an oil or fat, the glycerides are decomposed with the liberation of glycerin and the formation of an alkali

salt of the fatty acid, *i.e.*, a soap. The reaction may be represented in the following manner:

$$\underbrace{\text{Fatty acid} + \text{glycerin}}_{\text{Fat or oil.}} + \text{alkali} = \underbrace{\text{fatty acid} + \text{alkali}}_{\text{Soap.}} + \text{glycerin.}$$

House-fat recovered from garbage is also employed extensively for the making of high-grade soaps. In the manufacture of candles from tallow, the solid stearin is separated from the liquid olein; the former is utilized for candles, while the latter is converted into soap, and forms an excellent stock for this purpose. It is also extensively used for the oiling of wool. Soaps are also made from the recovered grease obtained from scouring liquors; as a rule, this material can only be made into a very low grade of soap, unless well purified before saponification. Rosin is also capable of being used as a soap stock as it combines with alkalies to form a saponaceous body in a manner similar to oils and fats. Rosin, or colophony, is the residue left after distilling oil of turpentine from natural rosin. It is seldom employed by itself for soap-making, but is only added in small amounts to other soap stocks; most of the so-called bar soaps contain varying amounts of rosin. It gives a dark brown color to the soap, which also retains its peculiar resinous odor. The use of rosin in scouring soaps is a mooted question, but no especial benefit can be seen in its use; whereas, on the other hand, it is liable to form insoluble products which are difficult to remove from the fibers, it being especially sensitive to hard water. Hence its presence in a textile soap, for woolen material at least, should be regarded as an adulteration.

A good scouring soap should be free from filling materials of all kinds, among which may be listed silicate of soda, flour, starch, etc. These are added for the purpose of giving an apparently hard dry soap, which may be loaded down with an excessive amount of water.

The consensus of opinion from the best authorities on the subject is that a good scouring soap should be neutral; carbonated alkali is cheap compared with soap, and if its addition is desired by the scourer it can be added in the proper amount to the scouring bath when needed. The manufacturer in buying soap should not be made to pay a soap price for an accompanying amount of carbonated alkali. The soap should be especially free from caustic alkali, for reasons which have already been thoroughly discussed. It should not contain any unsaponified fat or free fatty acid, as just so much of the soap is needed to emulsify this, and hence it will be the less efficient in scouring. It should also be free from rosin, mineral oil, and all other unsaponifiable matter; and finally it should be free from sodium silicate and any other filling material.

Olein soap, unless manufactured from purified stock, is very apt to contain petroleum and mineral oils, which do not saponify. It is also liable to contain iron which gives it a blackish color; this is due to the practice of allowing the olein to cool and settle in iron vessels. Olein also dissolves lead, and this is liable to give the material scoured

with it a grayish color, which is very difficult to subsequently remove.

Soaps prepared from potash as the alkaline base are much more soluble in water than the corresponding soaps prepared from a soda base. The best potash soaps, however, will only contain about 44 percent of fatty acid, whereas a good soda soap will contain as much as 66 percent of fatty acid. As the percentage of fatty acid present in a soap may be taken as a measure of its strength, it will be seen that a potash or soft soap has about two-thirds the strength of a soda or hard soap, and on this basis the potash soap is much more expensive than the soda soap. Although the soaps prepared from different oils will have different degrees of solubility, it may be stated in general that soda soaps on an average will require about 1000 parts of water to dissolve 20 parts of soap.

It is said that the solubility of soda soaps may be increased by the addition of small quantities of cresol; 20 parts of soda soap mixed with 5 parts of cresol, it is claimed, will dissolve in 100 parts of water at 105° F., and furthermore, this solution may have added to it 125 parts of a 10 percent solution of soda ash without precipitation of the soap. A mixture of 20 parts of soda soap (with 66 percent fatty acid) with 5 parts cresol is said to be equivalent in scouring value to 30 parts of potash soap (with 44 percent fatty acid), and that the cresol is not more costly than the soap; it is even said that the cresol adds to the scouring of the soap, by itself being a detergent.[1]

2. Manufacture of Soap.

Hard soap may be made by one of three general processes:

(a) By boiling the oil and alkali together under ordinary pressure.

(b) By boiling the oil and alkali together in closed vessels, and under pressure.

(c) By mixing the oil and alkali at the ordinary temperature, which gives the so-called *cold process* soap.

The first method is the one most commonly employed, and it is also the usual method for the manufacture of soft soap. The boiling of the oil and the alkali is continued until the former is completely saponified, that is, converted into soap. The point at which this occurs is usually determined by dissolving a sample of the product in water, when, if it is completely soluble without leaving any residue of oil, the process is judged to be finished. In the case of hard soaps, after the saponification is completed, the melted mass of soap is run into a saturated solution of common salt, and as the soap is insoluble in this solution, the curd separates out from excess of alkali, water and glycerin. The curd is collected, melted, and cast into bars or other forms as desired. The salt liquor remaining is known as *spent lye* and is further treated for the recovery of the glycerin it contains.

It may be roughly stated that 100 pounds of oil or fat will require about 100 pounds of caustic soda lye of 32° Tw. for a complete saponification by this method, though some oils, like cocoanut oil, will require more. In the practical manufacture of hard soap by this proc-

[1] F. Raschig, *Ger. Pat.* 86,560 of 1895.

ess it is customary to start with a lye of about 10° Tw., about 3 gallons being used to each 100 lbs. of fat, and frequently a small amount of scrap soap is added for the purpose of starting the saponification. After the first lot of fat and lye have been well boiled together, a lye of about 18° Tw. is added in the proportion of 10 gallons for each 100 pounds of fat. In the last stages of the boiling a still stronger lye of about 25° Tw. is used.

In the process of soap-making by boiling under pressure, the fat and alkali are simply boiled for several hours at a pressure of about 60 to 65 pounds, after which the melted mass is run out and cooled. As there is no salting out, the soap contains all of the ingredients, consequently, in order to work this process successfully, it is necessary to use just the proper amounts of fat, alkali and water.

The cold process of soap-making is very simple in procedure. The fat is melted and mixed with a strong lye and allowed to stand until saponification is complete, when the soap is ready for use. The saponification by this process requires several days but the cost of the operation is cheaper than with the other methods, and the yield of soap is larger, as all of the material used in its manufacture remains therein. As it is almost impossible, however, to secure complete saponification of all the fat used in this process, the soap so obtained always contains more or less free fat, and it will also, as a rule, contain a considerable amount of free alkali. The presence of the free fat may lead to the soap becoming rancid, and such a soap possesses the additional disadvantages of "sweating" and drying up when exposed to the air.

Cold-process soap dissolves, however, more freely in water than boiled soap, and consequently lathers better; it is also more desirable for use with hard water. Cocoanut oil is largely used for the making of cold-process soap, owing to the fact that it saponifies very easily with concentrated lyes, and yields a soap of good color that dissolves readily and lathers well. Tallow, palm oil, and castor oil are also extensively used for the manufacture of cold-process soaps. The fat or oil used in the making of a cold-process soap should be fresh and pure and free from uncombined fatty acids. The alkali should also be of the best grade, and it is usually employed at a strength of 70 to 72° Tw., and containing 32 to 33 percent of actual caustic soda. Cocoanut oil and cotton-seed oil saponify best with a lye of 72° Tw., while tallow, palm oil, and some other fats, work best with a lye at 66° Tw. If cocoanut oil is used, 100 pounds of the oil will require 50 pounds of lye at 72° Tw.; cotton-seed oil will require somewhat less; tallow, palm oil, and other fats require about 50 pounds of lye at 66° Tw. On the above basis the finished soap should contain about 25 percent of water.

Soft soaps, as already mentioned, are made from caustic potash; their method of manufacture being very simple. The fat or oil is boiled with the alkali until saponification is complete, after which the soap is run out and allowed to cool, when it is ready for use. Though the process is rather simple in principle, yet it is difficult to carry out at times in practice. The principal oils used for the manufacture of soft soap are linseed oil, whale oil, cotton-seed oil and olive oil. Linseed

oil saponifies readily, and gives a good, pale, transparent soap, free from odor. Fish oils give dark colored soaps with a fishy odor. Cotton-seed oil gives a good, pale, transparent soap. Olive oil yields a dark green colored soap. Tallow is sometimes added in small quantities to soft soaps in order to make them "fig."

A fig soap is one which has small granules resembling fig seeds throughout its mass, hence the name. It is said to be due to the presence of sodium stearate which crystallizes out when the soap becomes cool. The lower grades of cotton-seed oil and olive oil contain large proportions of stearin, and are liable to "fig" strongly, whereas the better grades of oil give clear, transparent soaps.

White soft soaps may be prepared from tallow and cocoanut oil, with lard or other fat, giving a white soap. In the making of soft soap, as a rule, 100 pounds oil will require about 200 pounds of caustic potash at 32° Tw. A good soft soap should contain about 42.5 percent of fatty acid, 10 percent of potash, and 47.5 percent of water. Soft soaps are sometimes cheapened by the addition of rosin, in which case it is best to saponify the rosin by itself, and then add the rosin soap so formed to the soft soap. In the making of rosin soap, 100 lbs. of rosin are boiled with 50 pounds of soda crystals ($Na_2CO_3 10H_2O$) dissolved in a small quantity of water. The amount of rosin which may be added to a soft soap is from one-seventh to one-tenth that of the fat used.[2]

The following table summarizes the characteristics of the soft soaps produced with different oils:

Oil.	Soap.
Linseed oil	Dark amber color, with pleasant odor.
Whale oil.	Dark reddish color, with fishy odor.
Cotton-seed oil.	Golden to amber color, varying with refinement of oil; no odor when freshly prepared, but apt to become rancid on keeping.
Olive oil.	Amber to greenish color, of fine quality.
Lard.	Fine white soap.
Hemp-seed oil.	Green color.
Cocoanut oil.	Fine white soap.
Tallow.	Stiff white soap, apt to "fig."

The following table gives the scouring power (or water-softening power) of various soaps:

Soap made from	Scouring Power.
Pure stearic acid	100.0
Pure oleic acid	100.0
Lard oil	96.0
Tallow	95.6
Bone fat (on 100 percent fat)	95.6
Myristic acid	93.3
Olive oil	93.2
Rosin 1 part, tallow 3 parts	92 4
Cotton-seed oil	87.0

[2] According to Theis (*Strangbleuche*) a rosin soap suitable for kier-boiling of cotton is made by boiling 100 parts of rosin and 25 parts of caustic soda with 1,000 parts of water. Use indirect steam for heating and boil for 4 to 5 hours From carefully conducted experiments in the washing of cloth it has been shown that the use of soaps without rosin gives the purest white. Trotman also claims that soaps containing sodium silicate give an inferior white as compared with those prepared from pure fatty acids.

Soap made from	Scouring Power.
Palm oil (crude)	85.0
Palm oil (bleached)	85.0
Neatsfoot oil	85.0
Rape oil	79.0
Cocoanut oil	79.0
Arachnis oil	78.5
Maize oil (corn oil)	76.2
Butter fat	69.5
Sperm oil (saponifiable)	68.0
Sesame oil	67.5
Rosin (saponifiable)	65.0
Rosin (crude)	58.0
Wool-grease (saponifiable)	37.0
Linseed oil	35.5

According to an experiment by Shukoff and Scheztakoff [3] the washing power of various soaps is in the following decreasing order: tallow soaps, soaps from liquid vegetable oils and olein, cocoanut and palm oil soaps, rosin soaps. They also show that the concentration of the soap solution has great influence on the scouring power, and solutions of 0.2 to 0.4 percent give the greatest washing effect, whereas concentrations greater or less than this have a lesser effect. The fact that the greatest emulsifying power is given by soap solutions of the above concentration has also been shown by Spring [4] and by Donan and Potts.[5] The proper concentration is about a one three-hundredth normal solution, and is explained as being due to the effects of contact electrification. When the concentration passes a certain value, the positively charged sodium ions of the soap exercise a coagulating action on the negatively charged oil particles, and consequently the emulsifying power is decreased. A similar effect is shown by Harrison [6] in the case of sodium oleate on the contact difference of cotton, the maximum charge being given with a N/200 solution.

3. Analysis of Soaps.

As already pointed out under the discussion of soaps for scouring purposes, a soap consists essentially of a salt of soda or potash with a mixture of various fatty acids, together with varying quantities of carbonated or caustic alkalies, and a considerable amount of water. In some soaps (cold-process and soft soaps) there is also present glycerin, and in some cases free fatty acids. A pure neutral soap is one which does not contain any free alkali (either as carbonated or caustic alkali) or free fatty acid. Most soaps, however, to be found in trade will have small quantities of carbonated alkali, at least, if not some caustic alkali.[7]

[3] *Chem. Zeit.*, 1911.
[4] *Koll. Chem.*, 1909, p. 161.
[5] *Koll. Chem.*, 1910, p. 208.
[6] *Jour. Soc. Dyers & Col.*, 1911, p. 283.
[7] In sampling a soap for purposes of analysis, care should be taken to obtain as representative a sample as possible. When the soap is in the form of a bar or cake, it is best to cut a sample from across the middle of the bar; or a cylindrical sample may be taken from the bar by means of a cork-borer or cheese sampler. Under no circumstances should the sample for analysis be taken exclusively from either the outer or inner portions of the soap, as these may differ considerably from one another in their amount of moisture and other constituents.

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carbonated and as caustic alkali. The total free alkali may be determined by taking 100 c.c. of the soap solution (containing 50 gms. per liter), precipitating out the soap by adding a saturated salt solution and titrating the filtrate with N/10 sulfuric acid, using phenolphthalein as the indicator.[10] The result will be the sum of both carbonated and caustic alkali.[11] A qualitative test for free alkali may be made by placing a drop of phenolphthalein solution on a freshly-cut surface of the soap; if a red coloration appears, free alkali is present.

(*e*) *Caustic Alkali.*—This may be determined as just described above in the solution of the soap in absolute alcohol. The method, however, is not very satisfactory, as if any water is present some of the carbonated alkali will be dissolved, and so to be accurate, the sample of soap should be previously dried before being dissolved in the alcohol; on the other hand, if the alcohol is quite absolute (that is, does not contain any water) some of the caustic soda will remain undissolved.[12] Another, and perhaps better, method of determining the amount of caustic alkali is the following: To 100 c.c. of the

[10] This method, though largely used in technical practice, is open to severe criticisms. In the first place, what is known in trade as "free alkali" in soaps is generally understood as caustic alkali, as this is the only really objectionable form for the existence of the free alkali in soap to be employed for scouring In the preparation of scouring baths, soda ash is nearly always added in connection with the soap, and the amount of free soda ash which may at times be found in soap as free alkali would be small in proportion to that intentionally added to the scouring liquors. Of course the presence of free soda ash in a soap tends to raise the percentage of total alkali and might give a wrong impression in the analysis as to the real value of the soap, but this is corrected by the percentage of fatty acids found to be present, and which would gauge the actual amount of true soap in the sample under examination. Again, if there is a small amount of soda ash present in the soap, a false idea of the character of the soap might be given by reporting this as "free alkali," when the latter term would be taken to mean caustic alkali. Many soaps are made without the use of soda ash, simply from caustic soda and fats, and in such soap the amount of free alkali as determined above, might be taken to truly represent the amount of caustic alkali present It would be well to first make a qualitative test on the soap to discover if carbonated alkali is absent or present, which may be done by adding a drop of hydrochloric acid to a freshly cut surface of the soap; if any effervescence is noticed carbonated alkali is present, otherwise it is absent. If the latter is the case, then the free alkali as above determined may be safely reported as caustic alkali, but if carbonated alkali is found to be present, then it will be better to determine the caustic alkali separately as given in the next test. Another criticism which may be advanced against the method of determining free alkali by titration with acid and phenolphthalein, is that it really only gives the amount of caustic alkali plus one-half the amount of carbonated alkali which may be present; so in order to determine the true amount of carbonated alkali present, it is really necessary to make not only this determination, but to further determine the amount of caustic alkali in the soap; then by subtracting the latter from the total free alkali, one-half of the carbonated alkali is obtained, and this has to be multiplied by 2 in order to give the true amount of sodium carbonate in the soap.

[11] The details are given as follows (Schuttig, *Chemist-Analyst*, 1920): A sample of about 10 gms. is accurately weighed in a 150 c.c. beaker and dissolved in about 125 c.c. of distilled water (free from carbon dioxide), and then transferred to a 250 c c. graduated flask; 40 gms. of sodium chloride are weighed out, dissolved in 100 c c. of distilled water, and slowly added to the soap solution, agitating the flask well. Cool and make up to the mark with pure water and add 10 c.c. extra to compensate for the volume occupied by the precipitate of soap. Mix thoroughly and filter. Take 50 c c. of the clear filtrate and titrate with N/10 hydrochloric acid, with phenolphthalein indicator, until the pink color disappears and does not reappear on boiling.

[12] Wilson (*Chem. News*, vol. 59, 280) regards the determination of free caustic alkali in soaps as one of the most difficult analytical problems to be met with in practice. He claims that in high-class soaps which contain no free glycerides (*i.e.*, unsaponified fats) the alcohol method may be made to yield quite accurate results; but with soaps of a lower grade, where more or less unsaponified fats are present, the alcohol method is unsatisfactory, because just those conditions which are necessary to insure the stability of the soap (*i.e.*, the decomposition into an acid soap and free caustic alkali) are the same conditions to insure the absolute saponification of the glycerides by the free caustic alkali present. To one expert in soap analysis, the simultaneous presence of free alkali and free fats may be rather easily detected, for on the addition of alcohol with phenolphthalein the color at first becomes deep, then gradually fades, and may entirely disappear. The method for the determination of free caustic alkali based on the insolubility of the soap in strong brine solution, also does not give accurate results; nor does that method which depends on the precipitation of the alkali by means of carbon dioxide gas, the soap being dissolved in alcohol.

aqueous soap solution (containing 50 gms. per liter) there is added in slight excess a solution of barium chloride. This will cause the precipitation of all the soap and carbonated alkali as barium compounds; the caustic alkali will be unaffected and will remain in solution. The liquid is filtered, and the clear filtrate is titrated with N/10 hydrochloric acid and phenolphthalein, and the result will give the amount of caustic soda. Sulfuric acid should not be used in this titration, as there is present some barium chloride which would precipitate the acid. The carbonated alkali may be calculated by taking the difference between the total free alkali and the caustic alkali found, and multiplying by 2.

Another method for the determination of free alkali in soaps, and one also including the determination of free fats is given by Dieterich as follows: Dissolve one part of soap in 20 to 50 parts of water, and add so much sodium chloride to the solution that a little remains undissolved; this will cause the soap to be precipitated, and leave the free alkali in solution. The precipitated soap is filtered and washed with a little saturated salt solution. The mass on the filter is dissolved in water, and again salted out and filtered as before. The two filtrates are then combined and the free alkali determined by a titration with N/10 sulfuric acid and phenolphthalein. The soap left on the filter may then be dissolved in about 30 c.c. of absolute alcohol by warming on a water-bath, phenolphthalein added, and the free fats determined by titration with N/100 caustic potash, the result being calculated to oleic acid. As the alcohol frequently contains substances which decolorize phenolphthalein, it is necessary to determine separately the amount of N/100 caustic potash required to redden the phenolphthalein in 30 c.c. of alcohol and to subtract this figure from the former result.

(*f*) *Fatty Acids.*—A quick and convenient means of obtaining the amount of fatty acids [13] present in a soap, and one which is sufficiently accurate for most technical purposes, is the following: 100 c.c. of the soap solution (containing 50 gms. per liter) is placed in a beaker, and to it there is added 5 gms. (accurately weighed) of paraffin wax. An excess of sulfuric acid is then added, which causes the precipitation of the fatty acids as a flocculent mass.[14] The liquid is then heated to the boil until all of the fatty acids have become thoroughly incorporated with the melted paraffin, which floats on the top. The mixture

[13] The greater the amount of fatty acids (combined) present in a soap the more actual soap the sample contains. Any hard soap containing more than 64 percent of fatty acids has either been dried spontaneously by keeping, or has been dried artificially. Hard soaps containing less than that amount have been reduced intentionally, and may contain an excess of water or alkali, or other incorporated adulterants.

[14] Together with the fatty aids there will also be precipitated any rosin which may be present in the soap. To determine qualitatively if rosin is present, Gottlieb gives the following method: A small portion of the soap is dissolved in boiling water, a concentrated solution of magnesium sulfate is then added until the fatty acids are completely precipitated. The magnesium resinate which is formed will remain in solution. After boiling for several minutes, the solution is filtered and the hot filtrate is acidulated with dilute sulfuric acid. If rosin is present, the liquid will become turbid owing to the separation of the resin acids. In order to make sure that the turbidity may not be caused by volatile fatty acids, the boiling should be continued for half an hour.

The reaction of Liebermann-Storch for the detection of rosin is considered the most accurate. It is carried out as follows: the fatty acids are dissolved in acetic anhydride at a gentle heat and the solution cooled. Sulfuric acid of 1.53 sp. gr. (prepared by mixing 34.7 c.c. concentrated acid with 37.5 c.c. of water) is then carefully allowed to flow into the solution, when the presence of the smallest amount of resin acid will be indicated by the appearance of a reddish brown coloration. The color does not last for any length of time.

is then allowed to cool, and when the cake of paraffin containing the fatty acids[15] is completely hard, it is carefully removed from the beaker, pressed between filter paper to remove adhering water, and weighed. The increase in weight of the paraffin gives the amount of fatty acids.[16] More accurate results are obtained, if the paraffin mass is melted in a weighed porcelain crucible and carefully heated on a sand-bath until all moisture is removed, and then cooled and weighed. Multiplying the weight of the fatty acids by the factor 0.97 will give the amount of fatty anhydride. Another method for determining the fatty acids is to take 100 c.c. of the soap solution, as before, precipitate the fatty acids with a slight excess of acid, run the liquid into a separatory funnel, and add about 50 c.c. of carbon tetrachloride (ether or other solvents may also be used, but carbon tetrachloride is preferable). The mass is then shaken and warmed gently, if necessary, until all of the fatty acids have dissolved.[17] On standing, the two liquids separate, the heavier carbon tetrachloride being underneath the water and containing the fatty acids in solution. This solution is drawn off into a weighed dish or flask, and heated on a water-bath until all of the solvent has been evaporated. The residue of fatty acids is then weighed.[18]

(*g*) *Rosin.*—For the determination of rosin in a soap the precipitate of fatty acids is employed, for this will also contain the resin acids which are precipitated along with the fatty acids themselves. Gladding's method is carried out as follows: about 1 gm. of the mixed

[15] A rapid method for the estimation of the fatty acid and one admitting of a fair degree of accuracy, is the following: The soap solution is placed in a burette, where the fatty acids are thrown out by the addition of hydrochloric acid; the burette is then heated in a deep beaker of boiling water or in steam, and the volume of the melted fatty acids is read in c.c. This number divided by the factor 0.85 (the average specific gravity of the fatty acids at 100° C.) gives the approximate weight in grams.

[16] The weight thus found, although often reported as "fatty acids" should more accurately be termed "fatty matter," for it may not only contain the fatty acids, but also, neutral fat, wax, unsaponifiable matter, and rosin. If the soap contains any soluble fatty acids, these will remain dissolved more or less in the liquid and will not be taken up by the paraffin wax. As a rule, the amount of fatty acid which is soluble is so small as to be neglected, except where cocoanut and palm-nut oil soaps are under examination. In such a case it is better to work with concentrated solutions, or to add common salt which will precipitate the majority of the soluble fatty acids. A less accurate method, according to Lewkowitsch, is to titrate the aqueous solution with standard alkali until neutral to Methyl Orange, then to add phenolphthalein and to again titrate with N/10 alkali. The alkali used in the second titration may be calculated to caprylic acid (the chief soluble acid), the molecular weight of which is 144, and the amount so found may be added to the rest of the fatty acids.

In accurate soap analyses the fatty acids are usually reported as anhydrides. In order to obtain the latter from the weight of the fatty acids themselves, multiply by the factor 0.97.

[17] Schulze (*Zeits Anal Chem*, vol. 26, p. 27) recommends the following method for the accurate determination of the fatty acids in a soap: The weighed sample of soap is brought into solution with water in an Erlenmeyer flask, decomposed with dilute sulfuric acid, and the separated fatty acids dissolved out with ether. The aqueous solution is removed as completely as possible by means of a pipette, and the ether washed three or four times with fresh water, care being taken to remove the aqueous layer as completely as possible. After the last washing and drawing off of the water, a few drops of barium chloride solution are added, in order to precipitate as barium sulfate any free sulfuric acid which may be present. The amount of water being so small, the ethereal solution may be at once passed through a filter, and thereafter evaporated in order to obtain the fatty acids, which are then free from sulfuric and hydrochloric acids, and do not darken at 100° C.

[18] The following quick method has been recommended by Saupe (*Jour. Soc. Chem. Ind.*, 1890, p. 1072): Two grams of fine soap shavings taken from the interior of the sample to be tested are dissolved in 50 c.c. of water in a stoppered graduated flask, and 5 c.c. of dilute sulfuric acid (1·4) are added; then 54 c.c. of dilute ether are added, and the mixture well shaken and allowed to stand; 20 c.c. of the clear ethereal solution of the fats are then withdrawn with a pipette, placed in a small weighed beaker, and evaporated to dryness, and the residue weighed. The percentage of fat in the sample is then obtained by multiplying the weight of the residue by the factor 125.

rosin and fatty acids is dissolved in about 40 c.c. of 90 percent alcohol by gently warming. A drop of phenolphthalein is added and a solution of alcoholic potash until the solution acquires a permanent pink color. The solution is then cooled and made up with ether to 200 c.c. There is then added 1 gm. of finely powdered silver nitrate, and the mixture shaken vigorously for 20 minutes, when the precipitate consisting of the silver salts of the fatty acids will coagulate and separate out. 100 c.c. of the ethereal solution containing the dissolved silver resinate is measured off and shaken with 40 c.c. dilute hydrochloric acid, and the precipitated silver chloride is removed together with the acid liquid. The ethereal layer containing the liberated resin acid in solution is transferred to a weighed dish, the ether evaporated, and the residue weighed.[19] By Twitchell's method the determination of rosin is carried out as follows: From 2 to 3 gms. of the mixed fatty and resin acids are weighed out accurately and dissolved in 10 times their volume of absolute alcohol, and a current of dry hydrochloric acid gas is passed through the solution, the vessel containing it being kept cool by immersion in cold water. After about 45 minutes the solution will have become saturated with the gas, and the operation is finished. This treatment converts the fatty acids into esters, but does not alter the rosin. The solution is then allowed to stand for one hour, after which it is diluted with 5 times the volume of water and boiled until the aqueous solution has become clear. The mixture is then transferred to a separatory funnel and the acid layer run off, the remaining solution containing the fatty acid esters and the rosin is washed with water until the last trace of hydrochloric acid is removed; 50 c.c. of alcohol are then added, and the solution is titrated with standard caustic soda or potash, with phenolphthalein as the indicator. The resin acids combine with the alkali, while the fatty acid esters remain unchanged. Each c.c. of normal alkali used is equivalent to 0.346 gm. of rosin.

Grittner and Szilasi[20] propose the following method for the determination of rosin in soaps; based on the fact that if such a soap is dissolved in alcohol and a solution of calcium nitrate is added, calcium stearate, palmitate, and oleate will be precipitated, the rosin remaining in solution as does also a portion of the calcium oleate. Dissolve 2 gms. of the sample of soap in alcohol (5 parts alcohol and 1 part water); if the solution is acid neutralize with a small amount of ammonia. Then add a 10 percent alcoholic solution of calcium nitrate in excess, cool and filter. Wash the precipitate with alcohol, add a solution of silver nitrate in slight excess to the filtrate, and then dilute with three volumes of water. Filter off the precipitate consisting of the silver salts of rosin and oleic acid, wash with cold water, dry at 70 to 80° C., and then digest with ether. Filter the ethereal

[19] To estimate the amount of rosin in soaps, Boulez recommends the following procedure: 5 gms. of the soap are dissolved in 200 c.c. of boiling water, and silver nitrate solution is added as long as a precipitate is formed. The precipitate is filtered off, dried thoroughly, and extracted with ether which will dissolve the resinate of silver. This ethereal solution is collected, and the silver salt decomposed by the addition of hydrochloric acid. Filter, wash with ether, and evaporate the filtrate in a weighed glass, and finally weigh the residue of rosin.

[20] *Chem. Zeit.*, vol. 10, p. 325.

solution of silver resinate, add dilute hydrochloric acid to the filtrate and shake. This liberates free rosin which dissolves in the ether; draw off the ethereal solution, evaporate to dryness and weigh the residue of rosin.[21]

4. Scouring Value of Soap.

The quality and value of a soap may be judged from its amount of fatty acid, combined alkali, and free alkali.[22] If much of the latter is present (especially if existing as caustic alkali), the soap is not a suitable one for use in scouring; and from the amount of fatty acid and combined alkali may be told the true amount of actual soap present in the sample.[23]

[21] Muter (*Analytical Chemistry*, p. 203) gives the following method for the determination of rosin in a soap: 10 gms. of the soap are dissolved in warm water, heated to boiling, and the fatty acids thrown out by excess of hydrochloric acid The acids are collected and washed with boiling water until free from all trace of acidity. They are then transferred to a narrow vessel, and kept melted therein until any contained water has completely settled out 0.5 gm. of these acids is then weighed out and dissolved in 50 c.c. of carbon tetrachloride, and placed in a 500 c.c. flask with a glass stopper, to this is then added 0.5 c.c. of bromine dissolved in 50 c.c. of carbon tetrachloride, and the flask is placed in a dark place for 18 hours. The flask is then cooled on ice, and a short piece of india-rubber tubing having been slipped over the neck so as to form a well around the stopper, this receptacle is filled with water, and the stopper is carefully opened, so that the water is sucked into the bottle without loss of hydrobromic acid vapor. The introduction of water is continued until 25 c.c. have been run in, and the flask is then well shaken. Some potassium iodide is added together with 75 c.c. more of water and some starch solution as an indicator, just sufficient sodium thiosulfate solution is added until the color is entirely removed. The contents of the flask are then transferred to a separator, and the aqueous portion is run therefrom (through a filter if necessary) into a porcelain basin and titrated with N/10 caustic soda, using Methyl Orange as the indicator, the c.c. of caustic soda used multiplied by the factor 1.6 gives the "bromine substitution" figure. This figure for the fatty acids found in commercial soaps is practically nil, while that of rosin as usually employed in soap manufacture, is 105. Therefore the bromine substitution figure divided by 1.05 gives the percentage of rosin in the fatty acids, and this result multiplied by the percentage of fatty acids already found in the soap and divided by 100 will give the percentage of rosin in the sample.

[22] Deess gives the following rapid method for the analysis of a soap for commercial purposes. Weigh out 10 gms. of the soap and dissolve in 100 c.c. of strong alcohol, then pass carbon dioxide gas through the solution in order to convert any free caustic alkali into carbonate, and then filter the solution. The free alkali in the soap being now in the form of carbonate is not dissolved by the alcohol and remains on the filter. This is washed with warm alcohol, then the precipitate is dissolved in warm water and is titrated with N/10 hydrochloric acid with Methyl Orange as the indicator The number of c.c. of acid used multiplied by the factor 0.0053 gives the amount of free carbonate in the 10 gms. of soap. The combined alkali and the fatty acids are now estimated by titrating the alcoholic solution, diluted with a little distilled water, with a normal solution of hydrochloric acid, using Methyl Orange as the indicator. The number of c.c. of acid used multiplied by the factor 0.031 gives the amount of combined alkali as Na_2O in the 10 gms. of soap, and multiplied by the factor 0.280 gives the amount of fatty acid. This latter factor is only for soaps made from olive oil; in case the soap is made from other oils or fats, it is first necessary to determine the saponification equivalent of the fatty acids of the soap.

[23] Wilson (*Chem. News*, 1891, p. 205) gives the following method for the analysis of soap, where there is a possibility of both free caustic alkali and free fatty acids existing simultaneously: (a) The total alkali is determined by titration with standard acid in the usual manner; (b) Another weighed quantity of the soap is decomposed in an Erlenmeyer flask on the water-bath with a slight excess of dilute sulfuric acid, the flask being kept on the water-bath until the fatty acids separate clear. The flask is then placed in ice-water to cool, and the liquid is then filtered. The fatty acids are washed three times successively with 250 c.c. of boiling water and allowed to cool each time and filtered. The united filtrates are diluted to one liter, and 500 c.c. placed in a beaker and tinted with Methyl Orange; N/10 alkali is then added until the liquid acquires the usual color, after which a little phenolphthalein is added, and the addition of the alkali continued until a permanent pink is established. The number of c.c. of alkali used in the last titration are due to the soluble fatty acids, and are calculated to caprylic acid. The fatty acids in the flask and any left on the filter are dried and weighed, and then dissolved in alcohol, and titrated with N/2 alkali The alkali so used, together with that required for neutralization of the soluble acids, and deducted from the total alkali, gives the alkali existing in other forms than as soap. If desired the soap may be decomposed with standard acid, and the alkali required to neutralize the Methyl Orange noted. This, deducted from the total acid used, gives the acid equivalent of the alkali existing in all forms. In this manner there is estimated:

The scouring value of a soap, in fact, is primarily determined by the amount of fatty acid (combined) that it contains. This is due to the fact that the amount of combined fatty acid present measures the amount of actual soap in the sample. The character of the fatty acid also has considerable bearing on the scouring value of the soap. as this will determine the lathering quality and emulsifying property of the soap solution.

It must be borne in mind that when soap is dissolved in water it undergoes partial dissociation, and it is presumed that many of the soap molecules are split up into free fatty acid and free caustic alkali. This accounts for the fact that a soap solution reacts alkaline with phenolphthalein (red color). The more dilute the soap solution the more will be the dissociation and consequently the greater will be the alkalinity. Very concentrated soap solutions are almost neutral. On the other hand it must also be borne in mind that a soap solution (even though very dilute) does not act the same as a simple mixture of water, fatty acid and caustic alkali.

The relative scouring values of different samples of soaps may be estimated with some degree of truth by a process somewhat after the manner of determining the soap-destroying power of a hard water. The test is carried out as follows: 5 gms. of the soap are dissolved in 300 c.c. of alcohol and diluted to 500 c.c. with water. A solution of calcium chloride (corresponding to 1 gm. of calcium carbonate per liter) is used: 10 c.c. being diluted with 60 c.c. of distilled water, and titrated with the soap solution until a permanent lather is obtained. By adopting a standard soap for comparison, the relative values for other soaps may be thus obtained. As a standard there may be used a neutral sodium palmitate prepared from 36 c.c. of N/10 solution of caustic soda and 0.921 gm. of palmitic acid.

The following method has also been suggested for grading soaps as to their scouring values: 1 gm. of neutral sodium palmitate (prepared as above described) is dissolved in 200 c.c. of water, and portions of 10, 20, 30, and 40 c.c. respectively of this solution are diluted to 50 c.c. with boiling water and tested in the apparatus described herewith (see Figure 300). The latter consists of a pipette, A, with a capillary outlet of about 0.45 mm., opening from a flat horizontal surface of about

(a) total alkali; (b) combined alkali; (c) insoluble fatty acids; (d) soluble fatty acids. The following example is given to illustrate the method:

Sample of French Scouring Soap.

Total alkali by titration was found to be 7.037 percent.
Weight of soap taken was 5 889 gms.
Weight of insoluble fatty acids was 2.005 gms.
N/2 alkali to neutralize, 18 05 c c. = 9 025 c c. normal
N/10 alkali to neutralize soluble acids 10 77 c c — 1 07 c c normal
Total alkali used for both soluble and insoluble acids = 10 0 c c. normal.

Hence, $\frac{10.0 \times 0.031 \times 100}{5.889} = 5.32$ percent combined alkali. Therefore the total analysis would be:

Total alkali	7 037	percent
Combined alkali	5 32	"
Uncombined alkali	1 72	"
Insoluble fatty acids	34 06	"
Soluble fatty acids (caprylic)	2.6	"
Total fatty acids	36.66	"

10 mm. in diameter. The pipette holds 5 c.c. and has a spherical body; the internal diameter of the stem is 3 mm. The receptacle for the oil to be used in the test may be a test-tube, but it is preferable to use a vessel of the form B, C, so as to obtain a more nearly constant pressure. This tube is immersed in a beaker containing water which is kept boiling. In using the apparatus, 2 to 3 c.c. of water are introduced into B, followed by 20 c.c. of kerosene oil. The pipette is rinsed out twice with the given soap solution, then filled and its point placed in the kerosene, and the number of drops formed in falling from the mark on the pipette noted. The number of drops given by each of the different boiling standard solutions with the standard kerosene oil is then plotted into a curve, in which the ordinates represent percentages of the standard, and the abscissæ the corresponding number of drops.

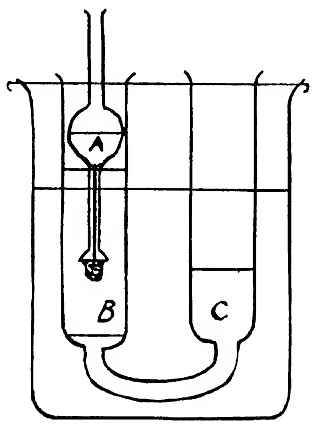

FIG. 300.—Apparatus for Determining the Scouring Value of Soap.

Unknown samples of soap are tested in the same manner and the results referred to sodium palmitate as the standard. Thus, if 0.5 gm. of a commercial soap be dissolved in 100 c.c. of water and the solution tested at the boiling point, it may be stated that the sample yields the same number of drops as a solution of sodium palmitate containing an equivalent scouring value. In testing cold water soaps, a solution of 1 gm. of sodium oleate in 200 c.c. freshly boiled distilled water is taken as the standard, or 100 percent. This method is based on the fact found by experiment [24] that when a solution of a soap is made to form drops beneath the surface of an oil, the number of drops formed from a given volume of the solution is dependent on the amount of soap present in the solution; and furthermore, the conclusion was reached that the number of drops formed was a measure of the emulsifying power of the given soap solution, and that the latter might stand as a measure of the detergent power of the soap. The following

[24] *Jour. Amer. Chem. Soc*, 1903, p. 1256.

figures are given by the originator of this method in testing the standard soap solution:

(a) Hot water test.

Full	standard	gives	average	of	268	drops,
0.8	"	"	"	"	228	"
0.6	"	"	"	"	179	"
0.4	"	"	"	"	119	"
0.2	"	"	"	"	56	"
Water	"	"	"	"	19	"

(b) Cold water test.

Full	standard	gives	average	of	153	drops,
0.8	"	"	"	"	140	"
0.7	"	"	"	"	128	"
0.6	"	"	"	"	123	"
0.5	"	"	"	"	111	"
0.4	"	"	"	"	106	"
0.3	"	"	"	"	84	"
0.2	"	"	"	"	51	"
0.1	"	"	"	"	25	"
Water	"	"	"	"	11	"

5. Mineral Oils in Soap.

Mineral oils may sometimes be present in a textile soap and a determination of the amount of the same may at times be desirable. The estimation of the mineral oil in a soap may be carried out as follows: A solution of a definite quantity of the soap in alcohol is evaporated to dryness with sand (purified by extraction with hydrochloric acid); the mass is wrapped in a filter-paper and extracted in a Soxhlet with chloroform. This reagent will dissolve out all mineral oil, but will not dissolve the dried soap. The chloroform solution is evaporated to dryness in a weighed beaker and the residue is weighed. In case there is any free fat in the soap, this will also be extracted with the chloroform, and it will then be necessary to saponify the fats by boiling with an alcoholic solution of caustic soda, evaporating to dryness with sand, and extracting again with the chloroform.

6. Sodium Silicate as Soap Filler.

Sodium silicate is sometimes employed as a filler for soaps, due to the fact that a soap containing it may be loaded with considerable water without appearing moist. This adulteration may be estimated as follows: 5 gms. of the soap are placed in a porcelain crucible and ignited until all organic matter is burnt off; the residue will consist of the alkali together with any silicate that may be present.[25] The resi-

[25] Other fillers which are sometimes employed in soaps are the following: (*a*) *Sugar;* this is only liable to be present in transparent soaps, and even then, never in large amounts; it may be detected by the use of Fehling's test by acidulating the aqueous solution of the soap with sulfuric acid, filtering from the separated fat, then boiling the filtrate for half an hour. The solution is then neutralized with caustic soda, some Fehling's test solution added, and the mixture boiled, when a red precipitate of cuprous oxide will be formed if sugar is present in the soap. The amount of sugar may be estimated by employing a weighed amount of the soap and filtering off the cuprous oxide, drying, igniting, and weighing the resulting copper oxide; this multiplied by the factor 0.40875 gives the amount of sugar. (*b*) *Starch;* this may be detected by neutralizing the soap solution and adding a few drops of iodine solution when a blue color will develop in the presence of starch. The amount of starch may be determined in the same manner as employed above for the estimation of sugar, only the copper oxide obtained is multiplied by the factor 0.40816 to obtain the equivalent weight of starch. It is not likely that both starch and sugar will be present in the same sample of soap.

due is treated with hot water acidulated with hydrochloric acid, and then evaporated to dryness. It is again taken up with water and a little hydrochloric acid, which dissolves the alkali, or other mineral matter present, but will leave silicic acid, SiO_2, as an insoluble residue. This latter is filtered off, dried, ignited, and weighed. It is usually reported in terms of silicic acid, or silica, as it is called.[26]

7. Complete Analysis of Soap.

A scheme for the complete analysis of soap is given in the table on page 621. It includes the determination of all the constituents liable to be found in a soap.

Vulte[27] recommends the following scheme for a complete soap analysis: The soap to be examined is cut into ½ in. cubes, several of which are placed in a dry test-tube which is kept well corked. When portions are to be weighed-up, as many cubes as may be required are taken out and the loss in weight of the tube determined. Two or three cubes (5 to 10 gms.) are thus placed in a small leaden crucible containing 25 to 30 gms. of dry sand and a small glass rod, all weighed together; 50 to 75 c.c. of absolute alcohol are added, and the whole heated on the water-bath, stirring at intervals, until the soap is dissolved; the solution is then evaporated to dryness, the contents of the dish being thoroughly mixed as the drying proceeds, and finally dried in an air-bath at 100° C. until constant weight is reached. The loss in weight represents water and alcohol, and any essential oils which may be present as perfumes. The leaden dish is then bent up and placed in the inner tube of an extraction apparatus, and treated with petroleum ether for 1 to 2 hours so as to dissolve out all unsaponified fat. The residue is similarly treated with 95 percent alcohol for 1½ hours, whereby soap and glycerin are dissolved out. The insoluble residue is treated with water, and fractions of the solution tested for sodium chloride, sulfate, and silicate respectively.[28] Anything insoluble in water is examined for pigments, metallic soaps, wood-pulp, clay, silica, etc. The alcoholic solution is titrated for free caustic alkali with phenolphthalein as the indicator; water is then added, and the alcohol boiled off in a current of steam. Excess of normal hydrochloric acid is added, together with sodium chloride or sulfate to salt out the fatty

[26] The amount of *sodium chloride* in soap may be determined in the liquor obtained in the titration of total alkali with sulfuric acid. This liquid is filtered and neutralized with caustic soda. A few drops of potassium chromate solution are then added and the liquid is titrated with a normal solution of silver nitrate until a permanent reddish color is obtained; each c.c. of silver nitrate solution is equivalent to 0.0585 gm. of sodium chloride.

[27] *Jour. Soc. Chem. Ind.*, 1893, p. 630.

[28] Horn (*Zeits. f. d. Chem. Ind.*, vol. 16, p. 85) points out that the usual process of estimating the sulfate, chloride, and carbonate of sodium and potassium in soap by extraction with absolute alcohol, and testing the insoluble residue, leads to wrong results, since commercial absolute alcohol dissolves considerable quantities of those salts. Furthermore, the high percentage of water in soaps dilutes the alcohol, which also causes considerable amounts of the salts to go into solution in the alcohol, and which amount is always neglected. It is recommended to dissolve the soap in water, separate the fat with nitric acid and determine the chlorine in the filtrate with silver nitrate. For estimating sodium or potassium carbonate and sulfate, the soap must be dried for a long time at 30 to 40° C., after which the dry soap is treated with absolute alcohol, filtered, washed, and the residue on the filter dissolved in boiling water; one portion is titrated with standard acid in order to obtain the amount of carbonate, while another portion is precipitated with barium chloride to determine the amount of sulfate. A still better method is the direct determination of the carbonic acid.

Leed's Scheme for Soap Analysis

Weigh out 5 gms. Dry at 110° C. Loss = water.

Treat the dried soap with petroleum ether in a Soxhlet apparatus.

- Extract is free fat. Evaporate off the ether and weigh the residue fat.
- Residue consists of soap and mineral matter, treat with alcohol.
  - Extract is soap, free caustic alkali (and rosin and glycerin). Add a few drops of phenolphthalein, and titrate with normal sulfuric acid
    - c.c. H_2SO_4 used x 0.031 = Na_2O as caustic alkali. x 0.040 = NaOH.
    - Add excess of water and boil off the alcohol. Add a little Methyl Orange and titrate with normal sulfuric acid; c.c. H_2SO_4 used x 0.031 = Na_2O as combined alkali. Add slight excess of acid, boil, cool and filter off fat.
      - Evaporate filtrate to dryness on water-bath; take up with absolute alcohol; evaporate solution to dryness in a tared dish and weigh residue as glycerin.
      - Residue contains fatty acids and rosin. Dry at 110° C. and weigh; dissolve one-half in alcohol, add phenolphthalein, and titrate with normal alcoholic soda; from this calculate the saponification equivalent. Add ether and dry powdered silver nitrate. Shake well and allow to settle.
        - Ppt. of silver salts of fatty acid; may be neglected.
        - Solution contains silver resinate; filter, decompose with 20 c.c., dilute HCl, allow AgCl to settle; shake with some petroleum ether; separate ethereal layer; place in tared glass, evaporate, and weigh residue as rosin. This subtracted from combined weight of fatty acids and rosin gives fatty acids.
  - Residue is carbonate, chloride, sulfate, and silicate of sodium, with starch, and insoluble residue. Treat with little water and filter.
    - Filtrate contains Na_2CO_3, NaCl, Na_2SO_4, Na_2SiO_3. Divide into four equal parts.
      - Titrate with normal H_2SO_4, and calculate as Na_2CO_3.
      - Titrate with standard $AgNO_3$, or weigh as AgCl, and calculate as NaCl.
      - Precipitate with $BaCl_2$ and weigh as $BaSO_4$, calculate as Na_2SO_4.
      - Decompose with HCl and determine soda combined in silicate, and silica.
    - Residue is starch and insoluble matter; dry and weigh. Starch may be determined by application of Fehling's test.

acids of cocoanut oil, and the whole is boiled. After chilling to solidify the fatty acids, two holes are punched in the cake, and the acid watery liquid run off through a filter; the residual cake is boiled up with water and salt as before and the wash water added to the previous liquid. The unneutralized acid is then determined, thus giving the amount of alkali combined with the soap. The fatty acids are dissolved in ether and ultimately weighed, rosin being subsequently determined by either Gladding's or Twichell's methods.

8. Examination of Fatty Acids in Soap.

It is often required to obtain some information respecting the nature of the fats or oils which have been employed in the manufacture of a soap. This can only be done by a chemical examination of the fatty acids derived from the soap, and even then, the information is by no means satisfactory or definite. Considerable knowledge concerning the nature of the soap stock employed, however, may be derived from ascertaining the following chemical properties of the fatty acids. The fatty acids may be extracted from the soap by precipitating the solution with hydrochloric acid, then boiling the liquid to melt the fatty matters set free; and on cooling, removing the cake of fatty acids. This should be dried by melting in a porcelain dish and carefully heating until all moisture is removed.

(*a*) *Melting Point.*—A small capillary tube is prepared by drawing out a small piece of glass tubing made plastic by heating in a Bunsen flame. This is filled with the fatty acid by dipping it into the molten fat, and then allowing it to solidify and cool. The capillary tube is then attached to the stem of a thermometer by means of a small rubber ring. The thermometer is then immersed in a small beaker of water, which is itself contained in a larger beaker of water. The latter is gradually heated, while the thermometer is watched until the fat in the capillary tube melts, when the temperature is noted. The solidifying point of a fat is generally somewhat different from its melting point, and may be determined by melting the fatty acids in a test-tube, immersing a thermometer in the molten mass and stirring with the latter until the fats commence to solidify; at which point the reading on the thermometer will remain constant for a minute or two, and this is taken as the solidifying point.

(*b*) *Specific Gravity.*—This is usually determined at 100° C., and by the use of a small Sprengel's tube. The dry tube is first weighed, and then the weight filled with water (at about 15.5° C.) is taken. The tube is next filled with the melted fatty acids, and placed in the mouth of a wide-mouthed flask in which water is kept boiling. This brings the fats to a temperature of 100° C., which causes them to expand somewhat in the tube and the excess flows out from the latter. When the expansion ceases, all oil adhering to the tube is removed with a piece of filter paper, the tube is dried, cooled and weighed. The weight of the fats thus obtained, divided by the weight of the water gives the specific gravity of the fatty acids at 100° C. compared with water at 15.5° C.

(*c*) *Saponification Equivalent.*—By this is meant the amount of caustic potash required to saponify the fatty acids. It is obtained as follows: 5 gms. of the fatty acids are dissolved in about 60 c.c. of hot neutral alcohol, and titrated with normal alcoholic potash using phenolphthalein as the indicator. The weight of the fatty acids expressed in milligrams, divided by the number of c.c. of the potash required, gives the figure called the saponification equivalent.

By referring to the constants given below for the different oils and fats employed in soap-making, some idea may be obtained as the probable composition of the soap stock used for the manufacture of any sample of soap, after obtaining the above noted factors for its fatty acids.

SPECIFIC GRAVITY FACTORS

Oil or Fat	Sp. Gr.		Fatty Acids of Same.	
	15° C.	100° C.	15° C.	100° C.
Tallow	0.943	0.862	.....	0.8698
Lard	0.931	0.858	...	0.844
Palm Oil	0.922	0.8586	..	0.8369
Palm-nut Oil	0.952	0.8731	.....	......
Cocoanut Oil	0.930	0.8736	.....	0.8354
Olive Oil	0.917	0.862	.....	0.8759
Cotton-seed Oil	0.923	0.8725	.....	0.880
Linseed Oil	0.933	0.881	0.923	0.892
Castor Oil	0.965	0.9096	0.9509	0.896
Corn Oil	0.9203	0.8694	.....	......

MELTING POINT FACTORS

Oil or Fat	Melt. Point	Fatty Acids of Same
Tallow	42° to 46° C.	43° to 44° C.
Lard	40° to 42° C.	43° C.
Palm Oil	27° to 42° C.	50° C.
Palm-nut Oil	....	25° to 28° C.
Cocoanut Oil	20° to 28° C.	24° to 25° C.
Olive Oil	....	26° C.
Cotton-seed Oil	......	35° C.
Linseed Oil	....	20° C.

FACTORS FOR SOLIDIFYING POINT

Oil or Fat	Solid. Point	Fatty Acids of Same.
Tallow	36° C.	42° to 43° C.
Lard	27.1° to 29° C.	39° C.
Palm Oil	....	45.5° C.
Palm-nut Oil	20.5° C.	20° to 23° C.
Cocoanut Oil	16° to 20° C.	20° C.
Olive Oil	6° C.	21° C.
Cotton-seed Oil	0° to 1° C.	32° C.
Linseed Oil	16° to 20° C.	16° C.
Castor Oil	17° to 18° C.	3° C.
Corn Oil	10° C.	

Factors for Saponification Equivalent and Iodine Value of the Fatty Acids in Oils and Fats

Acids derived from	Saponification Equivalent	Iodine Value
Tallow	284	40
Lard	280	64.2
Palm Oil	270	..
Palm-nut Oil	211	12
Cocoanut Oil	196 to 206	9.3
Olive Oil	283	86 to 88
Cotton-seed Oil	286	115
Linseed Oil	307	179
Castor Oil	292	90

(*d*) *Iodine Value.*—This value (Hubl's) of the fatty acids is obtained in the following manner: 1 gm. of the fat is placed in a 500 c.c. stoppered flask and dissolved in about 10 c.c. of chloroform; 25 c.c. of an iodine-mercury chloride solution [29] is now run in, and the mixture well shaken. A clear solution should be obtained, otherwise more chloroform must be added. Should the deep brown color of the solution become discharged in a short time, 25 c.c. more of the iodine solution are added. The mixture is then allowed to stand in a dark place for 2 hours; 20 c.c. of potassium iodide solution [30] are now added, and the liquid shaken and diluted with about 300 c.c. of water; if a red precipitate of mercury iodide appears, more potassium iodide solution must be added. The excess of free iodine which has not combined with the fat is now titrated with a N/10 solution of sodium thiosulfate with a drop of starch paste as the indicator, the blue color of the solution being discharged as soon as sufficient sodium thiosulfate has been added. A blank test is then made on 25 c.c. of the original iodine solution, and the difference between the two titrations shows the amount of iodine absorbed by the fat, and this is calculated into percentage on the weight of the fat taken, and termed the iodine value.

9. Comparison of Different Soaps.

In order to furnish some data for comparison in the analysis of soaps, the following analyses of commercial soaps are given:

No. 1 is a potash or soft soap made from olive and cotton-seed oils.
No. 2 is a potash soap made from olive oil and tallow.
No. 3 is a potash soap made from olive oil alone.
No. 4 is a potash soap made from cotton-seed oil.
No. 5 is a potash soap made from unknown source.
No. 6 is a gray mottled soda soap made from a mixture of bone tallow, cotton-seed oil, and other fats.
No. 7 is a soda soap for milling made from tallow.
No. 8 is a soda soap for milling made from tallow and palm oil.
No. 9 is a soda soap for milling made from tallow-cotton-seed oil, etc.
No. 10 is a soda soap for scouring made from palm oil and whale oil.

[29] This solution is prepared by dissolving 25 gms. of iodine in 500 c.c. pure alcohol and 30 gms. mercuric chloride in the same amount of alcohol, and mixing the two solutions. The solution should be allowed to stand at least 12 hours before use, and as it even then gradually loses its strength, it must be titrated at the time of use.

[30] This solution is prepared by dissolving 100 gms. of potassium iodide in 1000 c.c. of water.

No. 11 is a soda soap for scouring made from olive oil.
No. 12 is a soda soap for scouring made from tallow and cotton-seed oil.
No. 13 is a soda soap for softening made chiefly from palm oil or palm oil with oleic acid.
No. 14 is an American soda soap made from cotton-seed oil.
No. 15 is a French soda soap made from olive oil.

Constituents.	1	2	3	4	5
Water	42 20	37.10	48.75	41.78	45.95
Combined alkali	9.20	10.08	7 32	9.05	7.78
Fatty acid anhydrides	43.78	47.50	38.37	43.82	40.36
Free alkali as carbonate	0.82	1.58	2.05	1.40	
Free alkali as hydrate	0.45	0.28	0 22	0.15	1.50
Free fats	....	....	...	....	....
	6	7	8	9	10
Water	30.17	26.73	29 53	23.25	25 38
Combined alkali	6.15	7.98	7.78	8.57	7.31
Fatty acid anhydrides	62.65	67.22	64.05	69.50	65.40
Free alkali as carbonate	0 42	0.18	0 26	0.12	0.75
Free alkali as hydrate		.	.	..	....
Free fats	0.34	. .	. .	....	....
	11	12	13	14	15
Water	20.56	18.55	66.80	27.94	33.86
Combined alkali	7 07	7 98	3.15	6 81	5.19
Fatty acid anhydrides	64.11	72.60	25 95	63 24	59.91
Free alkali as carbonate	0 35	0 42	0.15		
Free alkali as hydrate	...	....	1.05	0.45	0.44
Free fats				0.67	0.36

A good, well-made soft soap should contain about the following proportions among its constituents:

	Percent
Water and glycerin	47.3
Combined alkali	6.8
Fatty acids	45.3
Free alkali	0.6

The following is the analysis of a yellow laundry soap containing rosin:

	Percent
Water	19.26
Combined alklai	8.57
Free alkali as caustic	0.20
Free alkali as carbonate	0.20
Fatty acid anhydrides	52.32
Rosin	19.45

The table on pages 626, 627 presents in a condensed form the chief characteristics and analytical factors of the various oils and fats employed in the making of textile soaps.

Soaps to be used in connection with hard water are nearly always made from cocoanut oil, or a mixture of fats in which this oil forms a large proportion. Soaps made from cocoanut oil will give a good lather even with water possessing considerable hardness. Shaving soaps and sea-water soaps also are made with a large proportion of cocoanut oil.

Name of Oil.	Source.	Chief components.	Specific grav. at 15.5° C.	Solidification point. °C.	Saponification equiv.	Lbs. KOH to saponify 100 lbs. of oil.	Lbs. NaOH to saponify 100 lbs. of oil.	Other characters.
Animal Origin. Bone Fat	Bones of various animals.	Olein and palmitin.	0.0915	....	284-294	19.1-19.7	13.6-14.1	Brown color, unpleasant odor.
Lard	Abdomen of pig.	Olein, palmitin, and stearin.	0.860 at 99° C.	27-44	286-292	19.2-19.6	13.7-14	
Lard Oil	By pressing lard.	Olein.	0.915	−4 to + 10	290	19.3	13.8	
Tallow	From cow and sheep.	Stearin, palmitin, and olein.	0.856 at 99° C.	33-48	283-290	19.3-19.8	13.8-14.2	Varies greatly in composition.
Tallow Oil	By pressing tallow.	Olein.	0.916	0 to 6	288-292	19.2-19.4	13.7-13.9	Resembles lard oil.
Whale Oil	Blubber of whale.	Olein and valerin.	0.920-0.931	....	250-296	18.9-22.4	13.5-16	Yellow color, fishy odor.
Vegetable Origin. Castor Oil	Seeds of castor oil plant.	Ricinolein.	0.958-0.970	−18	302-319	17.6-18.1	12.6-13.1	Very viscous.
Cocoanut Oil	From cocoanut.	Laurin, palmitin, and stearin.	0.868-0.874 at 99° C.	14-23	209-228	24.6-26.8	17.6-19.2	Consistency of butter. Used in "marine" soaps.

Cotton-seed Oil	From seeds of cotton plant.	Olein, stearin, and linolein.	0.916-0.930	1-10	267-294	19.1-19.7	13.6-14.1	Fatty acids melt at 38° C.
Hemp-seed Oil	From seeds of hemp.	Linolein.	0.925-0.932	—15 to —28	290	19.3	13.8	Similar to linseed oil.
Linseed Oil	From seeds of flax.	Linolein.	0.931-0.937	—20 to —27	288-300	18.7-19.5	13.3-13.9	A drying oil.
Olive Oil	From olives.	Olein.	0.914-0.917	—6 to +4	286-303	19-19.5	13.3-13.9	
Palm Oil	From fruit of palm tree.	Palmitin and olein.	0.920-0.945	20-36	277-286	19.6-20.2	14-14.4	Of variable composition.
Rape-Seed Oil	From rape-seed.	Brassein.	0.911-0.917	—6 to —10	314-328	17-17.6	12.2-12.6	
Olein, or Oleic Acid	Pressing tallow of palm oil.	Oleic acid.	0.887-0.908	6-22	281-293	19.1-19.9	13.6-14.2	Of variable composition.
Rosin	Residue from distillation of crude terpentine.	Abietic acid, etc.	1.04-1.10	135	290-330	17-19 3	12.2-13.8	Used only with other oils for yellow soaps.

It appears that the comparative viscosity of solutions of soaps prepared from different oils indicates somewhat the nature of the fatty bodies from which the soap was prepared. Whitelaw [31] determined the point of dilution at which the following soap solutions ceased to form a jelly after standing for 24 hours:

Green olive oil	1 in 18 of water
Olive oil (old)	1 in 50
Cotton-seed oil	1 in 100
Palm-nut oil	1 in 150
1 rosin and 3 tallow, Tallow, Palm oil	1 in 200 to 250

The same observer also determined the viscosity of the various soap solutions by taking the time required for the solution to flow from a 50 c.c. pipette, from which water flowed in 28.2 seconds. The temperatures of the solutions were 50° F. The following were his results:

Soaps	Dilution for Uniform Time
Green olive oil	1 in 30
Green soap	1 in 120
Cotton-seed oil	1 in 320
Palm-nut oil	1 in 320
do.	1 in 700
Pale soap	1 in 700
Tallow	1 in 700
Palm oil	1 in 700

A so-called *spinning-test* has been recommended for the testing of fulling soaps. The test is supposed to show if the soap is capable of forming a solution having the necessary body for fulling purposes. Cut 10 gms. of the soap in thin shavings and dissolve in 100 c.c. of water in a beaker heated in a water-bath. After the solution of the soap is completed, stand the beaker in cold water and stir the solution with a thermometer until it will draw out into threads. The temperature is noted and is called the "spinning temperature." It probably depends on the fusion points of the fatty acids of the soap but is independent of the amount of water. Nevertheless, the spinning temperature decreases much faster than the melting points of the fatty acids. The higher the spinning temperature the more suited is the soap for fulling. This temperature, however, may be raised by fillings, and it must be borne in mind that both sodium silicate and rosin are harmful in fulling soaps.

[31] *Jour. Soc. Chem. Ind.*, 1886, p. 90.

Chapter XXXI.

Testing of Materials Used in Bleaching; Acids.

1. Acids.

The principal acids employed in scouring and bleaching are *sulfuric, hydrochloric, acetic, formic, oxalic,* and *sulfurous.* As the latter, however, is used solely for its bleaching properties and not simply as an acid, its consideration will be taken up under the section on bleaching agents.

Acids are used principally as adjuncts in the bleaching of cotton and other vegetable fibers. In this case the material is treated directly with the dilute acid solutions which are known technically by the name of "sours," and the process is known as "souring." Acids are also used for the neutralizing of alkaline residues, as in mercerizing, when a weak acid bath is given after most of the caustic soda has been washed out of the cotton. An acid treatment is also sometimes given in cotton bleaching after the boil-out with soda for the purpose of cleaning up the material before entering the chemic bath. After a lime boil an acid treatment, or sour, is necessary to decompose the insoluble lime compounds in the fiber. Acids (particularly sulfuric) are also used in the peroxide bleaching process for the purpose of neutralizing the caustic soda produced by dissolving sodium peroxide in water. The use of acid solutions after a treatment with hypochlorite bleaching liquors (whether of lime or soda) is chiefly for the purpose of decomposing the residue of alkaline hypochlorite to form hypochlorous acid intimately in the fiber so as to increase its bleaching efficiency.

2. Sulfuric Acid.

This acid is also known as *oil of vitriol* or simply *vitriol.* It occurs as a heavy, oily, colorless liquid, containing a greater or less proportion of water. The chemical formula of sulfuric acid is H_2SO_4, and it is one of the strongest of the mineral acids. It is made at the present time by two distinct processes; the older method is known as the *lead chamber process,* and consists essentially in burning sulfur or a suitable sulfur compound, such as pyrites, whereby sulfur dioxide gas is formed; this is conducted through large chambers constructed of lead, where it is mixed with steam, air, and oxides of nitrogen. A chemical reaction takes place between these whereby the sulfur dioxide, SO_2, is oxidized to sulfur trioxide, SO_3, and this combines with the water present as steam, and gives sulfuric acid, H_2SO_4. A later method, but one which is now extensively used, is known as the *contact*

process; the sulfur dioxide gas being highly purified, mixed with air and passed over platinized asbestos (or other platinized material); the latter substance acting as a catalyzer to cause a combination to take place between the sulfur dioxide and the oxygen of the air with the formation of sulfur trioxide, and the latter combining with water, gives sulfuric acid. The contact process furnishes a highly concentrated acid, whereby the lead chamber process yields only a rather dilute acid which has to be concentrated by evaporation.

There are several commercial grades of sulfuric acid; *chamber acid* is a moderately concentrated acid and contains from 62 to 70 percent of pure acid, and has a density of 50° to 55° Bé.: *oil of vitriol* is a more concentrated acid, having a density of about 66° Bé. (168° Tw.), and contains about 93.5 percent of pure acid; *double oil of vitriol* (D. O. V.) has a further concentration, and contains about 96 to 98 percent of acid, though it has about the same density as the preceding (66° Bé.).

Sulfuric acid made from sulfur and by the contact process is generally freer from impurities than acid made from pyrites. The latter is liable to contain arsenic and its associated metals. Acid made by the chamber process is usually contaminated with lead. Acid brought into contact with organic matter soon develops a brown or blackish color due to the carbonization of the organic material.

Concentrated sulfuric acid will burn the skin or flesh very rapidly, so great care should be exercized in its handling. When poured into water sulfuric acid liberates a great amount of heat, which may cause the mixture to sputter and boil up, and so throw the acid out on the person handling it. In mixing strong sulfuric acid and water the acid should always be added to the water and gradually; water should never be poured on sulfuric acid, and the strong acid in no case should ever be poured into hot water.

Sulfuric acid is the widely used commercial acid, and is the cheapest, strongest and most important of the mineral acids. It dissolves most metals with the exception of lead and certain of the so-called "noble" metals, like gold, platinum, etc. Sulfuric acid of over 130° Tw. does not attack iron, so that strong acid may be safely shipped in tank cars and used in iron vessels. Strong sulfuric acid decomposes all the textile fibers; in dilute solution it does not injure the animal fibers (wool and silk), but it weakens the vegetable fibers, especially when the acid solution is allowed to dry into the material.

3. Qualitative Tests with Sulfuric Acid.

(*a*) *Mineral matter;* this may consist of sodium sulfate, gypsum, etc. Its presence is shown by ignition of a sample of the acid, when the residue should not be more than 1 percent. (*b*) *Iron;* this is tested for in the usual manner by diluting a portion of the acid with water and warming with a drop of nitric acid, then adding a few drops of a solution of potassium sulfocyanide, when a red color will be produced if iron is present; or instead, a few drops of a solution of potassium ferrocyanide may be added, which will give a blue color in the pres-

ence of iron. (*c*) ***arsenic;*** sulfuric acid is liable to contain this impurity from the iron pyrites used in its manufacture. To determine the presence of arsenic, dilute about 25 c.c. of the acid with 150 c.c. of water and treat with a current of hydrogen sulfide gas; if arsenic is present in any considerable amount, a yellow precipitate will be formed. A more delicate test is to dissolve a piece of pure zinc in a portion of the diluted acid, conduct the liberated hydrogen gas through a glass tube, ignite the gas as it emerges from the tube, and let the flame play against a cold surface of porcelain, the formation of a metallic mirror will indicate the presence of arsenic. (*d*) *Lead sulfate;* this is indicated by the formation of a white cloudiness when a sample of the acid is diluted with water; lead sulfate being soluble in concentrated sulfuric acid, but not in the dilute acid. (*e*) *Nitrogen acids;* these may be detected by taking about 5 c.c. of the acid in a test-tube, and carefully adding about the same amount of a solution of ferrous sulfate; the formation of a brownish purple ring where the two liquids meet will indicate the presence of nitrogen acids. (*f*) *Sulfurous acid;* this is liable to occur in the commercial sulfuric acid, and is undesirable on account of its bleaching action on many coloring matters. It may be detected by taking 5 c.c. of the acid, diluting to about 20 c.c. with water, and adding a drop of a dilute solution of potassium permanganate: if the latter is immediately decolorized, the presence of sulfurous acid is indicated. (*g*) *Organic matter;* this is indicated by the brownish color of the acid. Strong sulfuric acid left exposed to the air for any length of time will become brown in color, due to particles of dust and organic matter being absorbed by the acid and carbonized. In general, this impurity only consists of minute particles of carbon in suspension, and exerts no deleterious effect in the majority of cases where the acid may be employed.

4. Analysis of Sulfuric Acid.

The strength of this acid is generally determined by reference to its density, as is shown in the table given below. The total acid in a sample of sulfuric acid may also be determined by titration with a standard solution of alkali in the following manner: 25 c.c. of the sample is weighed in a beaker and then poured into about 500 c.c. of water; after cooling, the solution is diluted to one liter; 25 c.c. of this solution is then titrated with normal caustic soda, using Methyl Orange as the indicator; each c.c. of the alkali is equivalent to 0.049 gm. of sulfuric acid. Another method is to weigh out 1.082 gm. of pure sodium carbonate, dissolve this in water, and then run in from a burette the solution of sulfuric acid described above, using Methyl Orange[1] as the indicator; the number of c.c. of acid required for neutralization will contain exactly 1 gm. of sulfuric acid.

Example.—25 c.c. of sulfuric acid weighed 46 gms.; this was diluted to one liter, and it required 22.5 c.c. of the solution to neutralize 1.082 gm. of sodium carbonate; hence 22.5 c.c. of the acid contain 1 gm. sulfuric acid, or the liter contains 44.44 gms., and this on 46 gms. would be 96.6 percent.

[1] If the sulfuric acid being tested contains an appreciable amount of nitrous acid, Methyl Orange cannot be used as the indicator, unless the nitrous acid be previously removed by treatment with a small amount of potassium permanganate.

STRENGTH OF SULFURIC ACID SOLUTIONS (I)

Tw.°	Percent SO_3	Percent H_2SO_4	Kilos. per liter of H_2SO_4	Tw.°	Percent SO_3	Percent H_2SO_4	Kilos. per liter H_2SO_4
40	22.30	27.32	0.328	99	48.34	59.22	0.886
41	22.82	27.95	0.337	100	48.73	59.70	0.896
42	23.33	28.58	0.346	101	49.12	60.18	0.906
43	23.84	29.21	0.355	102	49.51	60.65	0.916
44	24.36	29.84	0.364	103	49.89	61.12	0.926
45	24.88	30.48	0.373	104	50.28	61.59	0.936
46	25.39	31.11	0.382	105	50.66	62.06	0.946
47	25.88	31.70	0.391	106	51.04	62.53	0.957
48	26.35	32.28	0.400	107	51.43	63.00	0.967
49	26.83	32.86	0.409	108	51.78	63.43	0.977
50	27.29	33.43	0.418	109	52.12	63.85	0.987
51	27.76	34.00	0.426	110	52.46	64.26	0.996
52	28.22	34.57	0.435	111	52.79	64.67	1.006
53	28.69	35.14	0.444	112	53.12	65.08	1.015
54	29.15	35.71	0.454	113	53.46	65.49	1.025
55	29.62	36.29	0.462	114	53.80	65.90	1.035
56	30.10	36.87	0.472	115	54.13	66.30	1.044
57	30.57	37.45	0.481	116	54.46	66.71	1.054
58	31.04	38.03	0.490	117	54.80	67.14	1.064
59	31.52	38.61	0.500	118	55.18	67.59	1.075
60	31.99	39.19	0.510	119	55.55	68.05	1.085
61	32.46	39.77	0.519	120	55.93	68.51	1.096
62	32.94	40.35	0.529	121	56.30	68.97	1.107
63	33.41	40.93	0.538	122	56.68	69.43	1.118
64	33.88	41.50	0.548	123	57.05	69.89	1.128
65	34.35	42.08	0.557	124	57.40	70.32	1.139
66	34.80	42.66	0.567	125	57.75	70.74	1.150
67	35.27	43.20	0.577	126	58.09	71.16	1.160
68	35.71	43.74	0.586	127	58.43	71.57	1.170
69	36.14	44.28	0.596	128	58.77	71.99	1.181
70	36.58	44.82	0.605	129	59.10	72.40	1.192
71	37.02	45.35	0.614	130	59.45	72.87	1.202
72	37.45	45.88	0.624	131	59.78	73.23	1.212
73	37.89	46.41	0.633	132	60.11	73.64	1.222
74	38.32	46.94	0.643	133	60.46	74.07	1.233
75	38.75	47.47	0.653	134	60.82	74.51	1.244
76	39.18	48.00	0.662	135	61.20	74.97	1.256
77	39.62	48.53	0.672	136	61.57	75.42	1.267
78	40.05	49.06	0.682	137	61.91	75.86	1.278
79	49.48	49.59	0.692	138	62.29	76.30	1.289
80	40.91	50.11	0.702	139	62.64	76.73	1.301
81	41.33	50.63	0.711	140	63.00	77.17	1.312
82	41.76	51.15	0.721	141	63.35	77.60	1.323
83	42.17	51.66	0.730	142	63.70	78.04	1.334
84	42.57	52.15	0.740	143	64.07	78.48	1.346
85	42.96	52.63	0.750	144	64.43	78.92	1.357
86	43.36	53.11	0.759	145	64.78	79.36	1.369
87	43.75	53.59	0.769	146	65.14	79.80	1.381
88	44.14	54.07	0.779	147	65.50	80.24	1.392
89	44.53	54.55	0.789	148	65.86	80.68	1.404
90	44.92	55.03	0.798	149	66.22	81.12	1.416
91	45.31	55.50	0.808	150	66.58	81.56	1.427
92	45.69	55.97	0.817	151	66.94	82.00	1.439
93	46.07	56.43	0.827	152	67.30	82.44	1.451
94	46.45	56.90	0.837	153	67.65	82.88	1.463
[illegible]	[illegible]	[illegible]	0.846	154	68.02	83.32	1.475

STRENGTH OF SULFURIC ACID SOLUTIONS (I) (*Cont.*)

Tw.°	Percent SO_3	Percent H_2SO_4	Kilos. per liter of H_2SO_4	Tw.°	Percent SO_3	Percent H_2SO_4	Kilos. per liter H_2SO_4
158	69.96	85.70	1.534	167.6	77.23	94.60	1.739
159	70.45	86.30	1.549	167.8	77.55	95.00	1.748
160	70.94	86.90	1.564	168	78.04	95.60	1.759
161	71.50	87.60	1.581	168.2	79.19	97.00	1.786
162	72.08	88.30	1.598	168.3	79.76	97.70	1.799
163	72.69	89.05	1.621	168.2	80.16	98.20	1.808
164	73.51	90.05	1.639	168	80.98	99.20	1.825
165	74.29	91.00	1.661	167.8	81.39	99.70	1.834
166	75.19	92.10	1.685	167.7	81.59	99.95	1.838
167	76.27	93.43	1.713				

The number of pounds per gallon (Imp.) may be found by multiplying the kilos. per liter by 10, or for U. S. gallon by 8.3.

STRENGTH OF SULFURIC ACID SOLUTIONS (II)

Bé.°	Percent SO_3	Percent H_2SO_4	Kilos. per liter H_2SO_4	Bé.°	Percent SO_3	Percent H_2SO_4	Kilos. per liter H_2SO_4
0	0.7	0.9	0.009	34	32.8	40.2	0.526
1	1.5	1.9	0.019	35	33.8	41.6	0.549
2	2.3	2.8	0.028	36	35.1	43.0	0.573
3	3.1	3.8	0.039	37	36.2	44.4	0.597
4	3.9	4.8	0.049	38	37.2	45.5	0.617
5	4.7	5.8	0.060	39	38.3	46.9	0.642
6	5.6	6.8	0.071	40	39.5	48.3	0.668
7	6.4	7.8	0.082	41	40.7	49.8	0.696
8	7.2	8.8	0.093	42	41.8	51.2	0.722
9	8.0	9.8	0.105	43	42.9	52.8	0.749
10	8.8	10.8	0.116	44	44.1	54.0	0.777
11	9.7	11.9	0.129	45	45.2	55.4	0.805
12	10.6	13.0	0.142	46	46.4	56.9	0.835
13	11.5	14.1	0.155	47	47.6	58.3	0.864
14	12.4	15.2	0.168	48	48.7	59.6	0.893
15	13.2	16.2	0.181	49	49.8	61.0	0.923
16	14.1	17.3	0.195	50	51.0	62.5	0.956
17	15.1	18.5	0.210	51	52.2	64.0	0.990
18	16.0	19.6	0.224	52	53.5	65.5	1.024
19	17.0	20.8	0.233	53	54.9	67.0	1.059
20	18.0	22.2	0.258	54	56.0	68.6	1.095
21	19.0	23.3	0.273	55	57.1	70.0	1.131
22	20.0	24.5	0.289	56	58.4	71.6	1.170
23	21.1	25.8	0.307	57	59.7	73.2	1.210
24	22.1	27.1	0.325	58	61.0	74.7	1.248
25	23.2	28.4	0.344	59	62.4	76.4	1.292
26	24.2	29.6	0.361	60	63.8	78.1	1.336
27	25.3	31.0	0.382	61	65.2	79.0	1.384
28	26.3	32.2	0.400	62	66.7	81.7	1.432
29	27.3	33.4	0.418	63	68.7	84.1	0.492
30	28.3	34.7	0.438	64	70.6	86.5	1.554
31	29.4	36.0	0.459	65	73.2	89.7	1.632
32	30.5	37.4	0.481	66	81.6	100.0	1.842
33	31.7	38.8	0.503				

5. Hydrochloric Acid.

This is principally known in trade as *muriatic acid,* and it has the formula of HCl. Hydrochloric acid is a gas under ordinary conditions, and the commercial liquid muriatic acid is a solution of the gas in water. It is obtained chiefly as a by-product in the manufacture of soda ash by the LeBlanc process, through the interaction of common salt (sodium chloride) with sulfuric acid. Hydrochloric acid dissolves in water with great readiness, forming a colorless solution which fumes in the air. The saturated solution of the gas has a density of 1.21 and contains 43 percent of acid. Hydrochloric acid is very reactive and dissolves most metals, as well as oxides and hydrates.[2] When mixed with nitric acid, it forms *aqua regia,* an acid capable of dissolving gold. Commercial hydrochloric acid usually has a density of 1.12 to 1.19, and is of a yellow color, which may be due to the presence of organic matter or of iron; it is also apt to contain some sulfuric acid and traces of arsenic; but for technical purposes it is generally pure enough.[3] The acid mostly met with in trade has a density of 1.16 (20° Bé. or 32° Tw.) and contains 32 percent of acid.[4] For some purposes of bleaching hydrochloric acid is to be preferred to sulfuric acid by reason of the fact that the former furnishes an easily soluble salt with lime, whereas sulfuric acid gives a highly insoluble calcium sulfate with lime compounds (calcium sulfate is soluble in 400 parts of water). On the other hand sulfuric acid is cheaper.

6. Analysis of Hydrochloric Acid.

(*a*) *For total acid;* the strength of hydrochloric acid for technical purposes is generally estimated by determining the density of the liquid, from which, by reference to the following table, the amount of acid may be calculated. If more accurate results are desired the acid may be titrated with a normal solution of caustic soda, using Methyl Orange as the indicator; each c.c. of normal caustic soda is equivalent to 0.0365 gm. of hydrochloric acid, HCl; 50 c.c. of the sample are weighed out, diluted to one liter, and 100 c.c. of this solution is titrated. (*b*) *For sulfuric acid;* take 100 c.c. of the sample diluted as above, nearly neutralize with sodium carbonate, then add a slight excess of barium chloride solution which will precipitate any sulfuric acid present as barium sulfate; this is filtered off, dried, ignited and weighed as $BaSO_4$. Each part of the latter is equivalent to 0.4206 gm. of sulfuric acid. (*c*) *For hydrochloric acid;* 100 c.c. of the acid solution as above is neutralized with sodium carbonate, a few drops of potassium chromate are added and the liquid is titrated with normal silver nitrate solution until a faint orange color is developed. Each c.c. of normal silver nitrate is equivalent to 0.0365 gm. of hydrochloric acid, HCl. (*d*) *For iron;* 100 c.c. of the acid solution as above is

[2] Hydrochloric acid attacks iron very vigorously and also attacks lead, therefore this acid cannot be transported in either iron or lead-lined containers. It is usually sold in glass carboys, or on a large scale, in special wooden tanks.

[3] In good commercial hydrochloric acid the content of sulfuric acid should not be more than 1 percent.

[4] The density in Tw.° approximately represents the percentage strength of hydrochloric acid; for example acid of 32° Tw. contains approximately 32 percent of HCl.

treated with a small piece of pure zinc, which causes the reduction of any iron to the ferrous condition; after the zinc has dissolved, a small amount of manganese chloride is added, and the solution is titrated with N/50 potassium permanganate, each c.c. of which is equivalent to 0.00112 gm. of iron (Fe) or to 0.0016 gm. of iron oxide (Fe_2O_3).

A good grade of commercial hydrochloric acid should not contain more than 1 percent of sulfuric acid, and an acid employed for bleaching should not contain more than 0.03 percent of iron. A qualitative test for iron may be made with potassium sulfocyanide solution (production of a red color) or with potassium ferrocyanide (production of a blue color). The presence of free chlorine in hydrochloric acid may be tested by dipping a strip of filter paper saturated with a starch and potassium iodide mixture in a sample of the acid; if the paper turns blue, the presence of free chlorine is indicated.

STRENGTH OF HYDROCHLORIC ACID SOLUTIONS (I)

Tw.°	Percent HCl	Gms. of HCl per liter.	Tw.°	Percent HCl.	Gms. of HCl per liter.
0	0.16	1.6	21	20.97	232
1	1.15	12	22	21.92	243
2	2.14	22	23	22.86	255
3	3.12	32	24	23.82	267
4	4.13	42	25	24.78	278
5	5.15	53	26	25.75	291
6	6.15	64	27	26.70	303
7	7.15	74	28	27.66	315
8	8.16	85	29	28.61	328
9	9.16	96	30	29.57	340
10	10.17	107	31	30.55	353
11	11.18	118	32	31.52	366
12	12.19	129	33	32.49	379
13	13.19	141	34	33.46	392
14	14.17	152	35	34.42	404
15	15.16	163	36	35.39	418
16	16.15	174	37	36.31	430
17	17.13	186	38	37.23	443
18	18.11	197	39	38.16	456
19	19.06	209	40	39.12	469
20	20.01	220			

It will be noticed that for each degree Twaddell density of hydrochloric acid solutions there is approximately one percent of acid present.

STRENGTH OF HYDROCHLORIC ACID SOLUTIONS (II)

Bé.°	Percent of HCl.	Bé.°	Percent of HCl.
0	0.1	17	26.6
1	1.5	18	28.4
2	2.9	19	30.2
3	4.5	19.5	31.2
4	5.8	20	32.0
5	7.3	20.5	33.0
6	8.9	21	33.9
7	10.4	21.5	34.7
8	12.0	22	35.7

STRENGTH OF HYDROCHLORIC ACID SOLUTIONS (II)—*Continued.*

Bé.°	Percent of HCl.	Bé.°	Percent of HCl.
9	13.4	22.5	36.8
10	15.0	23	37.9
11	16.5	23.5	39.0
12	18.1	24	39.8
13	19.9	24.5	41.2
14	21.5	25	42.4
15	23.1	25.5	42.9
16	24.8		

7. Acetic Acid.

This acid differs from the preceding in that it is not a mineral but an organic acid; that is, it is a carbon compound. At the present time acetic acid is chiefly obtained in the destructive distillation of wood, the crude acid being known as pyroligneous acid. This is saturated with lime and furnishes calcium acetate, which on distillation with sulfuric acid gives pure acetic acid. Acetic acid is also formed in the fermentation of various fruit juices, notably cider, which furnishes vinegar, the latter owing its acid properties to acetic acid.[5]

Acetic acid is usually sold in the form of a liquor of 1.041 specific gravity, or 8° Tw. (6° Bé.), and containing about 30 percent of actual acetic acid. A more concentrated form has a specific gravity of 1.0052, or 10° Tw., and contains 40 percent of acid. Glacial acetic acid is a pungent smelling liquid, having a density of 11.6° Tw., and containing about 98.8 percent of acid. The name of this acid is derived from the fact that on cooling it deposits crystals of pure acetic acid. Acetic acid is not as strong in its acidic properties as the mineral acids, but as it serves equally well for the neutralization of alkalies, it is extensively employed in bleaching for that purpose.

Commercial acetic acid is liable to contain the following impurities: Sulfuric acid and sulfates, hydrochloric acid and chlorides, iron, lead, and lime. The presence of free sulfuric acid or sulfates may be detected by the addition of a solution of barium chloride, when a white precipitate will be formed. Hydrochloric acid or chlorides is detected by the addition of a solution of silver nitrate when a white precipitate will be formed. Lime is detected by the addition of a solution of ammonium oxalate, which will form a white precipitate. Iron is detected by boiling a sample of the acid with a few drops of nitric acid and then adding a solution of potassium sulfocyanide, when a red color will be produced. Lead is detected by treating a sample of the acid with sulfuretted hydrogen, when a dark brown or black color will form. The dark color of some grades of acetic acid is due to the presence of organic or tarry substances. A good practical test for the presence of free mineral acids in acetic acid is to moisten strips of white calico with the acid, and dry these at 90 to 100° C. If mineral acid (sulfuric or hydrochloric) is present the calico will be tendered.

[5] Ordinary commercial grades of acetic acid contain from 6 to 15 percent of propionic and butyric acids. These acids are higher homologues of the same series as acetic acid, and as a rule do not interfere with the customary uses of the acetic acid, and in the analysis of acetic acid they are included in the general term of acid strength. Glacial acetic acid on the other hand contains very little, if any, of these other acids.

The strength of acetic acid may be determined by titration with standard alkali, using phenolphthalein as an indicator; 25 c.c. of the sample are weighed and diluted with water to 500 c.c.; 100 c.c. of this solution are titrated with normal caustic soda, each c.c. of the latter being equivalent to 0.060 gm. of acetic acid. For general purposes a chemical analysis is not required for acetic acid, as the density is taken to represent the amount of acid present. On account of the fact, however, that solutions of acetic acid above density of 1.055 show an anomaly between the density and the amount of acetic acid this method is of no avail for high percentages of acid, because densities above this point correspond to two solutions of different strengths. In order to tell if a certain acid (of higher density than 1.055) contains more or less than 77 percent of acid, a little water may be added, and the density again taken; if the density increases, the acid was stronger than 77 percent; if otherwise, the acid was weaker.

STRENGTH OF ACETIC ACID SOLUTIONS

Percent Acetic Acid	Sp. Gr.	Percent Acetic Acid	Sp. Gr.	Percent Acetic Acid	Sp. Gr.	Percent Acetic Acid	Sp. Gr.
0	0.9992	26	1.0363	52	1.0631	77	1.0748
1	1.0007	27	1.0375	53	1.0638	78	1.0748
2	1.0022	28	1.0388	54	1.0646	79	1.0748
3	1.0037	29	1.0400	55	1.0653	80	1.0748
4	1.0052	30	1.0412	56	1.0660	81	1.0747
5	1.0067	31	1.0424	57	1.0666	82	1.0746
6	1.0083	32	1.0436	58	1.0673	83	1.0744
7	1.0098	33	1.0447	59	1.0679	84	1.0742
8	1.0113	34	1.0459	60	1.0685	85	1.0739
9	1.0127	35	1.0470	61	1.0691	86	1.0736
10	1.0142	36	1.0481	62	1.0697	87	1.0731
11	1.0157	37	1.0492	63	1.0701	88	1.0726
12	1.0171	38	1.0501	64	1.0707	89	1.0720
13	1.0185	39	1.0513	65	1.0712	90	1.0713
14	1.0200	40	1.0523	66	1.0717	91	1.0705
15	1.0214	41	1.0533	67	1.0721	92	1.0696
16	1.0228	42	1.0543	68	1.0725	93	1.0686
17	1.0242	43	1.0552	69	1.0729	94	1.0674
18	1.0256	44	1.0562	70	1.0733	95	1.0660
19	1.0270	45	1.0571	71	1.0737	96	1.0644
20	1.0284	46	1.0580	72	1.0740	97	1.0625
21	1.0298	47	1.0589	73	1.0742	98	1.0604
22	1.0311	48	1.0598	74	1.0744	99	1.0580
23	1.0324	49	1.0607	75	1.0746	100	1.0553
24	1.0337	50	1.0615	76	1.0747		
25	1.0350	51	1.0623				

8. Oxalic Acid.

This acid is a dibasic organic acid and belongs to a different series than acetic and formic acids. It has the chemical formula

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} = H_2C_2O_4,$$

though the commercial product is a crystalline body having 2 molecules of water of crystallization, $H_2C_2O_4.2H_2O$.

Oxalic acid is made by fusing caustic potash with sawdust. It is readily soluble in water, 1 part dissolving in 8 parts of water at 70° F. and in 1/3 part of water at 190° F. Oxalic acid is rather strong in its acidic properties and is poisonous; it forms two series of salts, oxalates such as $K_2C_2O_4$ and binoxalates like KHC_2O_4. The sodium and potassium oxalates are soluble in water but calcium oxalate is very insoluble, on which account the addition of ammonium oxalate is frequently recommended for the correction of hard water. Oxalic acid is also frequently employed in bleaching for the removal of rust stains (of iron), for which purpose it is very efficient. It does not injure vegetable fibers in the manner of the mineral acids, though if a strong solution of oxalic acid is allowed to dry into cotton it is liable to cause tendering, supposedly due to the fact that the acid crystallizes in the fiber and produces a bursting strain.

The commercial crystal oxalic acid is usually of high purity. Its analysis may be carried out by titration with normal alkali, or the fact may be utilized that it reacts quantitatively with potassium permanganate, thereby decolorizing the latter and consequently a normal solution of potassium permanganate may be used for its titration.

9. Formic Acid.

This acid has of late years attracted considerable attention for use in dyeing and bleaching as a substitute for acetic and sulfuric acids. Formic acid belongs to the same series of compounds as acetic acid, being the first member of the series and having the formula H.COOH. It is a strong acid but is quite volatile on drying and does not injure cotton. The commercial product is usually a 40 percent solution of formic acid in water, although at times it may be supplied in strengths up to even 85 percent.

Chapter XXXII.

Testing of Materials Used in Bleaching; Bleaching Compounds.

1. Sulfurous Acid.

The chief compounds of sulfur which find a commercial application in bleaching are sulfur (sulfurous acid), sodium bisulfite, sodium hydrosulfite and sodium thiosulfate.

(*a*) *Sulfur.*—This is employed for the purpose of generating sulfurous acid gas by burning in the air, the sulfurous acid gas (sulfur fumes, or sulfur dioxide) being then used for the bleaching of wool. Sulfur occurs native, the principal source at the present time being the underground sulfur beds of Louisiana and Texas. It is also obtained from Sicily and most other volcanic regions. The commercial article is seldom for technical purposes.

(*b*) *Sulfurous Acid.*—This is obtained when sulfur or sulfides are burnt in the air. It is also obtained by heating copper turnings with sulfuric acid. Sulfurous acid, or sulfur dioxide, SO_2, is a colorless gas possessing a characteristic pungent odor. It can be liquefied under pressure, and is now prepared commercially in this form, being contained in stout iron cylinders. Sulfur dioxide is quite soluble in water, at 10° C., about 51 volumes of the gas being absorbed. In the solution there may be considered as being present true sulfurous acid, H_2SO_3, but this like carbonic acid cannot be isolated, as on evaporation or boiling of the solution the gas is gradually expelled. For purposes of bleaching, sulfur dioxide is usually prepared by the bleacher himself, either by burning sulfur in the air, or by the action of acids on solutions of sodium bisulfite. It can, however, be obtained in the form of a solution in water, or in the liquefied state, as already mentioned. Solutions of sulfur dioxide are analyzed in the same manner as those

STRENGTH OF SULFUROUS ACID SOLUTIONS

Density			Per-cent SO_2	Density			Per-cent SO_2	Density			Per-cent SO_2
Sp. Gr.	Tw.°	Bé.°		Sp. Gr.	Tw.°	Bé.°		Sp. Gr.	Tw.°	Bé.°	
1.0028	0.56	0.3	0.5	1.0221	4.42	3.0	4.0	1.0401	8.02	5.4	7.5
1.0056	1.12	0.7	1.0	1.0248	4.06	3.4	4.5	1.0426	8.52	5.7	8.0
1.0085	1.70	1.2	1.5	1.0275	5.50	3.8	5.0	1.0450	9.00	6.0	8.5
1.0113	2.26	1.5	2.0	1.0302	6.04	4.1	5.5	1.0474	9.48	6.4	9.0
1.0141	2.82	2.0	2.5	1.0328	6.56	4.4	6.0	1.0497	9.94	6.7	9.5
1.0168	3.36	2.3	3.0	1.0353	7.06	4.7	6.5	1.0520	10.40	7.0	10.0
1.0194	3.88	2.6	3.5	1.0377	7.54	5.0	7.0	1.0543	10.86	7.3	10.5

of sodium bisulfite, the amount of sulfurous acid being estimated by means of iodine and sodium thiosulfate solutions. The usual means, however, for determining the strength of solutions of sulfur dioxide is to refer to their densities. There is given on page 639 a table showing the percentages of sulfur dioxide in solutions of different densities. The percentage of aqueous sulfurous acid, H_2SO_3, may be obtained from these figures by multiplying by the factor 1.28.

2. **Sodium Bisulfite.**

This is employed very extensively in the bleaching of wool for the purpose of generating sulfurous acid gas by treatment with acids. Sodium bisulfite is formed by saturating a solution of soda ash with sulfurous acid gas, and it possesses the chemical formula $NaHSO_3$. When treated with strong acids the following reaction takes place:

$$NaHSO_3 + HCl = NaCl + SO_2 + H_2O.$$

Sodium bisulfite occurs in trade in the form either of a solution or of a white powdery solid.[1] The liquid usually has a density of from 38° to 40° Bé. (74° to 80° Tw.). The customary technical analysis of sodium bisulfite, either as liquid or solid, includes only a determination of the amount of sulfurous acid gas it is capable of generating. This estimation is carried out as follows: Take 1 gm. of the sample (or if a liquid use 20 c.c.) and dissolve in water, and dilute to 1 liter; 20 c.c. of this solution are stirred into 50 c.c. of a N/10 iodine solution. The excess of iodine is then determined by a titration with a N/10 solution of sodium thiosulfate. Each c.c. of iodine solution neutralized by the sodium bisulfite solution is equivalent to 0.0032 gm. of sulfurous acid gas, or sulfur dioxide, SO_2. The N/10 solution of iodine is prepared by dissolving 12.686 gms. of pure iodine and about 30 gms. pure potassium iodide in 250 c.c. of water; when the iodine has completely dissolved, dilute the solution to 1 liter. In the titration of the excess of iodine solution with sodium thiosulfate a solution of starch is used as the indicator, as described under the analysis of bleaching powder.

Commercial sodium bisulfite may contain on the one hand free sulfurous acid, or on the other hand, normal sodium sulfite.[2] In order to detect which is present, a few drops of Methyl Orange solution are added to the diluted solution of the sample; if the liquid acquires a red color, free sulfurous acid is present; whereas, if the liquid assumes a yellow color, normal sodium sulfite is present. To determine the amount of free sulfurous acid present, take 50 c.c. of the sodium bisulfite solution prepared as above, add a few drops of Methyl Orange

[1] The solid bisulfite is a white crystalline powder evolving rather a pronounced odor of sulfurous acid. It decomposes rather rapidly if exposed to moist air and is quite difficultly soluble, especially where it is desired to prepare concentrated solutions; on this account the liquid bisulfite is preferred by many users. Liquid bisulfite of 38° to 40° Bé. contains 24 to 25 percent of SO_2, while the powder bisulfite contains about 60 to 62 percent of SO_2, so that 100 parts of bisulfite powder are equivalent to about 260 parts of bisulfite liquid.

[2] The liquid containing free sulfurous acid is marketed in wooden containers or glass carboys; that containing free neutral sodium sulfite may be shipped in iron containers. Iron is a frequent contamination in commercial sodium bisulfite solutions and gives the solution a yellow color. Liquid of this character should not be used for bleaching purposes, as it is liable to produce stains, and if the bleached material is subsequently used for dyeing the resulting colors are apt to be dull.

solution, and titrate with N/10 caustic soda solution until the red tint is discharged. Each c.c. of soda required is equivalent to 0.0032 gm. of sulfur dioxide existing as free sulfurous acid. To determine the amount of normal sodium sulfite, Na_2SO_3, which may be present, take 50 c.c. of the sodium bisulfite solution, add a few drops of Methyl Orange solution, and titrate with N/10 sulfuric acid until the yellow color is discharged. Each c.c. of acid required is equivalent to 0.0031 gm. of alkali existing as sodium sulfite, or to 0.0063 gm. of sodium sulfite, Na_2SO_3.

Besides the extensive use of sodium bisulfite for bleaching, it is also employed at times for neutralizing excess of chlorine in materials bleached with chloride of lime or hypochlorites, in which case it is known under the name of *antichlor*.[3] The solution of sodium bisulfite, if kept in well closed vessels, appears to be somewhat more stable than the solid, for the latter on heating, or even on exposure to moist air, rapidly evolves sulfurous acid gas and suffers considerable deterioration in strength. Solutions of sodium bisulfite of greater density than 62° Tw. are liable to deposit crystals of the salt in cold weather, and hence, lose their strength.

The following table gives the strength of sodium bisulfite solutions of different densities.

STRENGTH OF SODIUM BISULFITE SOLUTIONS

Bé.°	Percent $NaHSO_3$	Percent SO_2	Bé.°	Percent $NaHSO_3$	Percent SO_2
1	1.6	0.4	21	16.5	10.2
3	2.1	1.3	23	18.5	11.5
5	3.6	2.2	25	20.9	12.9
7	5.1	3.1	27	23.5	14.5
9	6.5	3.9	29	25.9	15.9
11	8.0	4.8	31	28.9	17.8
13	9.5	5.7	33	31.7	19.6
15	11.2	6.8	35	34.7	22.5
17	12.8	7.8	37	38.0	23.6
19	14.6	9.0			

3. Hydrosulfites.

Sodium hydrosulfite is formed when solutions of sodium bisulfite are treated with zinc dust, and it has the formula $NaHSO_2$. It has a stronger reducing power than sodium bisulfite, and acts as a powerful bleaching agent. The salt is very unstable, and gradually decomposes even in solution, being oxidized to the bisufite. It cannot be isolated from its solution. Sodium hydrosulfite is usually prepared by the bleacher himself as wanted, though of late there have appeared on the

[3] Sodium bisulfite is also used at times in cotton bleaching as an addition to the kier-boil to prevent the formation of oxycellulose. Its value in this connection, however, is somewhat problematical. It is, however, used in connection with the permanganate bleach as an after-treatment for the purpose of reducing and removing the brown deposit of hydrated manganese dioxide. It is also a valuable agent for the stripping of dyed goods, being used in this case generally in connection with zinc dust, thus forming sodium hydrosulfite. The use of sodium bisulfite as an antichlor depends upon the following reaction:

$$NaHSO_3 + 2Cl + H_2O = NaHSO_4 + 2HCl$$

market several forms of hydrosulfite compounds of comparative stability, the most important is that obtained by combination of the sodium hydrosulfite with formaldehyde. In order to ascertain the strength of a solution of sodium hydrosulfite, the following procedure is recommended: 100 c.c. of a standard solution of indigo-sulfonic acid[4] are placed in a porcelain dish; the hydrosulfite solution to be tested is sucked up into a burette (pouring the solution into the burette would cause oxidation of the hydrosulfite and consequently an error in the results) and run into the indigo solution until the blue color disappears. The indigo solution is best prepared by treating 1 gm. of pure indigo powder with 6 gms. of concentrated sulfuric acid, stirring carefully with a glass rod and allowing to stand for about 5 hours at a temperature of about 120° F.; then dissolve in water and dilute to 1 liter. 100 c.c. of this solution is equivalent to 0.1 gm. of indigo. A good concentrated solution of sodium hydrosulfite should require 0.8 c.c. to decolorize the 100 c.c. of indigo solution, while a dilute solution should require 1.7 c.c. for the same purpose.

The following is a list of the more important stable hydrosulfite preparations at present on the market.

Name.	Maker.	Composition.	Employment.
1. Rongalite C .... 2. Hydrosulfite N F conc.. 3. Hyraldite C Extra......	Badische Hoechst Cassella	Sulphoxylate of soda-formaldehyde $NaHSO_2+CH_2O+2H_2O$	Discharges on dyed cottons.
4. Rongalite C W.......... 5. Hydrosulfite N F W conc 6. Hyraldite C W Extra....	Badische Hoechst Cassella	The same product as 1, 2, and 3, but with an addition of zinc oxide.	Discharges on wool.
7. Rongalite C simple.. 8 Hydrosulfite N F. 9. Hyraldite A	Badische Hoechst Cassella	The double compound of sulphoxylate of soda-formaldehyde and bisulfite of soda-formaldehyde $[NaHSO_2+CH_2O+2H_2O]+[NaHSO_3+CH_2O+H_2O]$.	Discharges on cotton.
10. Rongalite C W simple 11. Hydrosulfite N F W. 12. Hyraldite W	Badische Hoechst Cassella	The same product as 7, 8, and 9, but containing an addition of zinc oxide.	Discharges on wool.
13. Rongalite Special .... 14. Hydrosulfite N F Special conc 15. Hyraldite Special	Badische Hoechst Cassella	The same as 1, 2, and 3, but with an addition of a catalytic agent, such as Induline Scarlet.	Discharges on cotton.
16. Decroline .... 17. Hydrosulfite A Z . 18. Hyraldite Z	Badische Hoechst Cassella	The basic sulphoxylate of zinc-formaldehyde, insoluble in water, but soluble in acetic acid $(ZnOH)\ HSO_2+CH_2O$.	Stripping colors.
19. Hydrosulfite conc. powder .. ... .A.S F. .... 20. Blankit .... 21. Hydrosulfite conc. powder ..... I L B	Badische Badische Hoechst	Hydrosulfite of soda free from water.	For the setting of vats with indigo, the vat dyes, etc., and for bleaching certain animal and vegetable products.

4. Zinc Dust.

This substance is liable to contain zinc oxide and iron as impurities, and its valuation is based on the amount of metallic zinc it contains.

[4] Also known as Indigotine or Indigo Extract, it is the sodium salt of indigo-disulfonic acid. The free acid itself may also be used.

The analysis is conducted as follows: 0.662 gm. of the zinc dust are taken and mixed with 80 c.c. of a solution of potassium bichromate containing 25 gms. per liter, and with 10 c.c. dilute sulfuric acid; after ten to fifteen minutes a second similar addition of acid is made, and later a third, stirring from time to time; 10 c.c. of concentrated sulfuric acid diluted with its own volume of water is next added, followed by the addition of about 10 gms. of pure ferrous ammonium sulfate. The excess of ferrous salt is then determined by titration with the solution of potassium bichromate. The number of c.c. of bichromate employed in the titration added to the 80 c.c. originally used and multiplied by the factor 0.025 will give the amount in grams of potassium bichromate used; the number of grams of ferrous ammonium sulfate added multiplied by the factor 0.1255 will give the amount of potassium bichromate used up by the iron salt; this latter subtracted from the total bichromate used gives the amount reduced by the zinc present in the sample, and the latter figure multiplied by 100 gives directly the percentage of zinc in the sample.

Another method[5] for the analysis of zinc dust is the following: About 0.5 gm. of the sample is weighed out and placed in a stoppered 250 c.c. flask, and 25 c.c. water is added. The mixture is well shaken and then 7 gms. of ferric sulfate are added, and the shaking continued. In about 15 minutes, the zinc will have dissolved with the exception of impurities; 25 c.c. of strong sulfuric acid are then added, and the flask filled with water to the 250 c.c. mark. 50 c.c. of this solution, after dilution with 50 c.c. of water, are titrated with standard potassium permanganate solution. Each c.c. of normal permanganate is equivalent to 0.0325 gm. of zinc, Zn.

5. Sodium Thiosulfate.

This compound is also known as *sodium hyposulfite,* or simply as "hypo," and is largely employed in photographic work. It is used by the bleacher for removing traces of chlorine from material which has been bleached with chloride of lime. When used as an antichlor the following reaction takes place:[6]

$$2Na_2S_2O_3 + Cl_2 = 2NaCl + Na_2S_4O_6.$$

Sodium thiosulfate is usually obtained from alkali waste and is one of the by-products worked up from the residues in the LeBlanc method of manufacturing soda ash. It occurs in the form of crystals which are readily soluble in water. Its solution is decomposed by the addition of hydrochloric acid, sulfur being precipitated and sulfur

[5] Wahl, *Jour. Soc. Chem. Ind.*, 1897, p. 15.

[6] According to some authorities the reaction proceeds as follows:

$$Na_2S_2O_3 + 8Cl + 5H_2O = Na_2SO_4 + H_2SO_4 + 8HCl$$

The reaction with hypochlorous acid is given as follows:

$$Na_2S_2O_3 + 4HOCl + H_2O = Na_2SO_4 + H_2SO_4 + 4HCl$$

If the hyposulfite is in excess the liberated hydrochloric acid will decompose it with the formation of free sulfur:

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S.$$

Just which reaction takes place is no doubt a matter of conditions. From the fact that free sulfur is very often liberated in the use of sodium thiosulfate as an antichlor, it is to be presumed that there are also other side reactions taking place not indicated by either of the above two equations.

dioxide liberated. Sodium thiosulfate may be analyzed by titration with a N/10 solution of iodine, using starch paste as the indicator. Each c.c. of N/10 iodine solution is equivalent to 0.0158 gm. of $Na_2S_2O_3$ or to 0.0248 gm. of $Na_2S_2O_3.5H_2O$; the latter figure being given because the crystallized salt contains 5 molecules of water of crystallization, as indicated in the latter formula.

Sodium thiosulfate is not used much at the present time as an antichlor, being replaced by sodium bisulfite. The latter is preferred as it is not liable to liberate free sulfur and thus produce the so-called "sulfur stains" which sometimes occur with the use of sodium thiosulfate. According to W. Kind 100 parts of sodium thiosulfate neutralize 114 parts of chlorine, while 100 parts of sodium bisulfite neutralize only 68 parts of chlorine.

6. Chloride of Lime.

The principal chlorine compounds employed in bleaching are chloride of lime, sodium hypochlorite, liquid chlorine, and electrolytic hypochlorite liquors. *Chloride of lime* is technically known as *bleaching powder,* or *chemic.* The commercial product usually contains from 35 to 37 percent of available chlorine. By *available chlorine* is meant that which is capable of being used in bleaching, or which exists in the form of hypochlorous acid.[7] Chloride of lime is made by allowing chlorine gas to act on slaked lime. Commercial chloride of lime occurs as a yellowish white powder which possesses the odor of hypochlorous acid, and gradually takes up moisture from the air. It sometimes contains calcium chlorate as an impurity; but outside of the fact that this compound has no value as a bleaching agent, its presence is generally unimportant. Calcium hydrate and calcium chloride are also usually present. Bleaching powder may be analyzed by several different methods, based principally on the oxidizing power of the available chlorine present.[8]

(a) *Penot's method.*—In this method the solution of bleaching powder is titrated with a standard solution of sodium arsenite, the available chlorine oxidizing the latter to sodium arsenate. The process is carried out as follows: 7.10 gms. of the sample of bleaching powder are put in a small mortar and rubbed into a thin cream with water, after which it is washed into a liter flask and diluted to the mark with water and well shaken. Then 50 c.c. of the turbid liquid (correspond-

[7] The term "available chlorine" as applied to hypochlorite bleaching compounds is somewhat of a misnomer; what really is meant by the term is oxidizing power in units of nascent oxygen. In this connection 1 atom of chlorine is equivalent to 1 atom of oxygen ($HO.Cl = HCl + O$), which accounts for the fact that the content of chlorine in hypochlorites seems twice as high as it really is. For example when 100 parts of chlorine gas are absorbed in caustic soda solution there is formed sodium hypochlorite and sodium chloride:

$$2NaOH + Cl_2 = NaOCl + NaCl + H_2O;$$

one-half of the chlorine only resulting in hypochlorite. But if this solution is analyzed there will be found 100 parts of "available chlorine." The same is true with bleaching powder; this product usually shows a content of about 35 percent of "available chlorine" in the form of hypochlorite. As a matter of fact, only one-half of this amount of chlorine exists as calcium hypochlorite in a solution of bleaching powder, the other half presumably existing as calcium chloride, and the chlorine in the latter product does not enter into the reaction connected with the estimation of "available chlorine."

[8] A full discussion of the constitution and reactions of bleaching powder is given in Chapter XIII.

ing to 0.355 gm. of the sample) are withdrawn[9] and titrated in a porcelain basin with continual stirring with N/10 sodium arsenite solution, until the liquid ceases to give a blue color when a drop is placed with a glass rod on a filter paper moistened with a solution of potassium iodide and starch. Each c.c. of the sodium arsenite solution used is equivalent to 1 percent of available chlorine, or to 0.00355 gm. of chlorine.[10] N/10 solution of sodium arsenite may be prepared by dissolving 4.95 gms. of pure resublimed arsenious oxide and 10 gms. of pure sodium carbonate in 200 c.c. of water, boiling until solution is complete, then cooling and diluting to one liter. The solution may be checked by titration against a N/10 solution of iodine. The potassium iodide and starch paper employed as the indicator may be prepared by

Titration of Bleach Solutions

N/10 Arsenite c.c.	Available Chlorine			
	On 1 c.c. Sample		On 10 c.c. Sample	
	Gms. per Lit.	Ozs. per Gal.	Gms. per Lit.	Ozs. per Gal.
0.05	0.177	0.0235	0.0177	0.00235
0.1	0.355	0.0472	0.0355	0.00472
0.2	0.710	0.0944	0.0710	0.00944
0.3	1.065	0.1416	0.1065	0.01416
0.4	1.420	0.1888	0.1420	0.01888
0.5	1.775	0.2360	0.1775	0.02360
0.6	2.130	0.2832	0.2130	0.02832
0.7	2.485	0.3304	0.2485	0.03304
0.8	2.840	0.3776	0.2840	0.03776
0.9	3.195	0.4248	0.3195	0.04248
1.0	3.550	0.472	0.355	0.0472
2.0	7.10	0.944	0.710	0.0940
3.0	10.65	1.416	1.066	0.1416
4.0	14.20	1.888	1.420	0.1888
5.0	17.75	2.360	1.775	0.2360
6.0	21.30	2.832	2.130	0.2832
7.0	24.85	3.304	2.485	0.3304
8.0	28.40	3.776	2.840	0.3776
9.0	31.95	4.248	3.195	0.4248
10.0	35.50	4.720	3.550	0.4720
11.0	39.05	5.192	3.905	0.5192
12.0	42.60	5.664	4.260	0.5664
13.0	46.15	6.136	4.615	0.6136
14.0	49.70	6.608	4.970	0.6608
15.0	53.25	7.080	5.325	0.7080
16.0	56.80	7.552	5.680	0.7552
17.0	60.35	8.024	6.035	0.8024
18.0	63.90	8.496	6.390	0.8496
19.0	67.45	8.968	6.745	0.8969
20.0	71.00	9.440	7.100	0.9440

[9] There has been considerable discussion as to whether the insoluble residue in bleaching powder solutions should be included in the titration or not. Fresenius recommends that it be titrated with the rest of the solution, while other authorities take the opposite course, and say that as this insoluble portion is not utilized in practice, in a technical analysis it should be disregarded, in which case the bleaching powder solution should be allowed to settle and only the clear liquor drawn off for titration.

[10] The chemical reaction between arsenious acid and chlorine is as follows:

$$As_2O_3 + 4Cl + 5H_2O = 4HCl + 2H_3AsO_4$$

saturating a piece of filter paper with a solution made by boiling about ¼ gm. of starch, ¼ gm. of potassium iodide, and 1/10 gm. of sodium carbonate with 50 c.c. of water.

(b) *Bunsen's method.*—This is based on the oxidation of sodium thiosulfate with solutions of bleaching powder. On account of the fact, however, that it estimates the chlorine in both calcium hypochlorite and chlorate,[11] it is not as well suited to the analysis of bleaching powder as the preceding method. The process is carried out as follows: 25 c.c. of the bleaching powder solution prepared as directed above (corresponding to 0.1775 gm. of the sample) are diluted with about 200 c.c. of water, and 10 c.c. of potassium iodide solution and 5 c.c. of concentrated hydrochloric acid added.[12] It is then titrated with N/10 solution of sodium thiosulfate with the addition of a little starch solution; when the blue color in the starch disappears the titration is completed.[13] Each c.c. of the sodium thiosulfate used is equivalent to 0.00355 gm. of available chlorine, so if the above amount of the sample of bleaching powder is taken, by multiplying the number of c.c. of thiosulfate used by 2 will give the percentage of available chlorine present. The N/10 solution of sodium thiosulfate may be prepared by dissolving 24.8 gms. of pure crystallized sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$ in water and diluting to one liter. The solution may be checked by titration against a N/10 solution of iodine or a N/10 solution of potassium bichromate. The starch solution is best prepared by rubbing about ½ gm. of starch into a cream with a little water, then pouring into about 250 c.c. of boiling water, boiling for 15 minutes, and pouring off the clear solution for use.[14]

(*c*) *Gay-Lussac's Method.*—This is based on the use of a hydrochloric acid solution of arsenious acid (4.409 grams of As_2O_3 per

[11] If it is desired to estimate the amount of calcium chlorate in a sample of bleaching powder the following method of Fresenius may be used. It depends on the fact that hypochlorites react with lead acetate to form lead peroxide whereas the chlorate present is unaffected. To carry out the analyses 20 gms. of the bleaching powder are ground up with water and made up to one liter; after settling 50 c.c. (= 1 gm of bleach) are filtered off through a dry filter and mixed with an excess of lead acetate solution. There is first formed a white precipitate of lead chloride and lead hydroxide which gradually becomes yellow and then brown, liberating chlorine and passing into lead peroxide. After the precipitate has settled more lead acetate solution is added to make certain that the reaction is complete. Allow the mixture to stand in an open flask with frequent shaking until the smell of chlorine has disappeared (8 to 10 hours). Then filter and wash till neutral. Add sodium carbonate in slight excess to the filtrate to precipitate the lead and lime as carbonates. Filter and evaporate filtrate nearly to dryness, then transfer to a Mohr apparatus and distill with hydrochloric acid, passing the liberated chlorine into potassium iodide solution and titrating the free iodine with thiosulfate in the usual manner; one equivalent of iodine is equal to one equivalent of chlorate (Cl_2O_5).

[12] If acetic acid is used instead of hydrochloric the presence of chlorate is said not to affect the result.

[13] The chemical reactions involved are as follows:

$$Cl_2 + 2KI = 2KCl + I_2$$
$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

[14] In sampling commercial bleaching powder for analysis, care should be taken to obtain average and representative samples. This is usually done by running a sampling tube down through the cask of bleaching powder and then mixing thoroughly the sample of powder thus withdrawn. The strength of a cask of bleaching powder may exhibit considerable variation at different parts of the mass. In order to avoid loss in strength the samples should be kept in dry glass bottles in a cool dark place. Casks of bleaching powder should not be stored in a warm place, as this may cause liberation of chlorine gas and result in the breaking open or even explosion of the casks.

A simple test to detect the presence of iron in bleaching powder is to heat a small sample of the latter to about 120° F. If the smallest trace of iron is present the bleaching powder will assume a pinkish color, whereas in the absence of iron the powder will remain perfectly white.

liter) with indigo solution (sodium sulfindigotate) as an indicator. The solution of bleaching powder is prepared with 10 gms. of the sample per liter and this is titrated into 10 c.c. of the arsenious acid solution to which a few drops of indigo solution have been added. The titration is continued until the blue color has disappeared. As 10 c.c. of the arsenious acid solution correspond to 10 c.c. of chlorine gas (at 0° C. and 760 mm. pressure), in order to obtain the number of liters of chlorine gas corresponding to 1 kilo. of bleaching powder (Gay-Lussac or French chlorometric degrees) divide the c.c. of chemic solution used into 1000. This method is said to lack accuracy since the arsenious acid in dilute solution is slow in action and this makes the end-point of the titration rather uncertain.

A rapid technical method for the analysis of chemic solutions is recommended as follows (Sutton). 4.95 grams of pure finely divided arsenious acid are dissolved with the aid of gentle heat in about 15 c.c. of glycerin and then diluted with water to 1 liter; 25 c.c. are measured into a flask and 1 c.c. of indigo solution added. The turbid solution of bleaching powder is poured into a suitable burette and before it has had time to settle, is delivered with constant shaking into the blue arsenious solution until the color is just discharged.

Another rapid technical method especially adapted for use in bleach houses for the analysis of dilute chemic solutions and bleaching baths is the use of a standardized indigo solution. This is prepared from pure sodium sulfindigotate, using 3 grams of sulfuric acid per liter, which gives an intense blue solution. This must first be standardized by titration with a solution of chemic of known strength. It is convenient to have the indigo solution of such strength that 10 c.c. will be equivalent to 0.005 gm. of available chlorine. In testing the chemic liquor, 20 c.c. are placed in a graduated cylinder and then the indigo solution is added in small portions and well shaken until a greenish blue color persists. Every 10 c.c. of indigo solution used will be equivalent to 0.25 gm. of available chlorine per liter.

Bleaching liquors consisting of chloride of lime in solution (generally prepared by passing chlorine gas through milk of lime) may be analyzed in the same manner as given above for the estimation of the available chlorine in bleaching powder.

The table on page 648 gives the strength of bleaching powder solutions of different densities in terms of available chlorine.

While the strength of freshly prepared solutions of bleaching powder may be determined with suitable practical accuracy by the hydrometer test, this is not true of old solutions or of bleach baths which have been in use for some time and which have been freshened up with additional chemic. There is a gradual accumulation of neutral salts ($CaCl_2$) in the bath which keep up the hydrometer reading and yet which do not affect the bleaching value or the content of available chlorine. The only method of accurately testing the strength of such bleach liquors is to subject them to a chemical analysis for the determination of the amount of available chlorine.

A good sample of commercial chloride of lime should show a con-

Bleaching Powder Solutions

Tw.°	Available Chlorine Grams per Liter	Available Chlorine Ozs. per Gallon	Chloride of Lime Ozs. per Gal.	Tw.°	Available Chlorine Grams per Liter	Available Chlorine Ozs. per Gallon	Chloride of Lime Ozs. per Gal.
1/8	0.35	0.0465	0.16	9	26.62	3.5405	12.22
1/4	0.70	0.0931	0.32	10	29.41	3.9115	13.50
1/2	1.40	0.1862	0.64	11	32.68	4.3464	15.00
3/4	2.05	0.2727	0.94	12	35.81	4.7627	16.43
1	2.71	0.3604	1.24	13	38.71	5.1484	17.76
1 1/4	3.38	0.3495	1.55	14	42.31	5.6672	19.42
1 1/2	4.15	0 5520	1.90	15	45.70	6.0781	20.97
1 3/4	4.86	0.6464	2.23	16	48.96	6.5117	22.47
2	5.58	0.7421	2.56	17	52.27	6.9519	23.99
2 1/2	7.03	0.9350	3.22	18	55.18	7.3389	25.33
3	8.48	1.1278	3.89	19	58.33	7.7579	26.77
4	11.44	1.5215	5.25	20	61.17	8.1356	28.08
5	14.47	1.9245	6.64	21	64.50	8.5785	29.60
6	17.36	2.3088	7.97	22	68.00	9.0440	31.21
7	20.40	2 7132	9.36	23	71.50	9.5095	32.82
8	23.75	3.1588	10.90				

tent of about 37 to 38 percent of available chlorine. American chloride of lime in steel drums will frequently show a strength of 40 to 41 percent of available chlorine. These high-strength bleaching powders, however, are very disagreeable to handle as they readily evolve chlorine gas when the container is opened and the workmen who have to prepare the solutions are subjected to very obnoxious and injurious fumes. According to Lunge (*Handbuch der Sodafabrikation*), chloride of lime can be prepared in the laboratory containing as high as 43 percent of available chlorine and showing the following composition:

	Percent
Calcium Oxide (CaO)	38.9
Available Chlorine	43.13
Chlorine as Chloride	0.29 (= 0.44 percent $CaCl_2$)
Water	17.00
Carbonic Acid (CO_2)	0 42 (= 0.95 percent $CaCO_3$)

According to Ditz, a commercial sample of bleaching powder was made up as follows:

	Percent
Available Chlorine	40.40
Free Lime (CaO)	4.90
Calcium Carbonate ($CaCO_3$)	4.45
Calcium Chloride ($CaCl_2$)	0.35
Water	17.56

A completely saturated bleaching powder of the formula

$$Ca\langle^{OCl}_{Cl}.H_2O$$

should show a content of 48.9 percent of available chlorine. A hypochlorite of lime of very high strength (80 to 90 percent of available chlorine) can be prepared by saturating a milk of lime liquor with

chlorine, evaporating under vacuum and filtering off the separated crystals from the mother liquor.[15] This material, however, has never been made commercially available.

The strength of bleaching powder solutions may be expressed either in terms of chlorometric degrees, as is customary in France, or in percentages of available chlorine, as is usual in England, America, and Germany. The chlorometric degrees gives the number of liters of available chlorine (measured at 0° C. and 760 mm. pressure) contained in 1 kilo. of bleaching powder. To convert chlorometric degrees into percentages of available chlorine, multiply by the factor 0.3178, and to change percentages of available chlorine into chlorometric degrees multiply by the factor 3.12. The following table gives the relation between the two systems:

Chlorometric Degrees	Percentage of Available Chlorine	Chlorometric Degrees	Percentage of Available Chlorine
63	20.22	100	31.78
70	22.24	105	33.36
75	23.83	110	34.95
80	25.42	115	36.54
85	27.06	120	38.13
90	28.60	125	39.72
95	30.19	128	40.67

The strength of chloride of lime may also be determined in the following manner by the use of hydrogen peroxide; the principle of the method depending on the fact that on treatment with a hypochlorite solution hydrogen peroxide instantly liberates an amount of oxygen equivalent to the amount of available chlorine in the hypochlorite. Dissolve 7.917 gms. of the chloride of lime in water and dilute to 250 c.c.; 10 c.c. of this solution are placed in the flask of a nitrometer and mixed with an excess, say 2 c.c., of commercial hydrogen peroxide; the solutions are mixed by shaking and the volume of gas evolved is measured in the usual manner.[16] The whole operation only requires 1 to 2 minutes. Every c.c. of gas evolved corresponds to 1 percent of active chlorine when working with the weight of chloride of lime given above.[17] This method of analysis may also be applied to other hypochlorites.

It is sometimes desirable to determine the amount of free lime present in solutions of bleaching powder. This may be done by the addition of sodium sulfite to the solution which decomposes the hypochlorites present and forms sodium sulfate; the free lime is subsequently titrated in the presence of phenolphthalein with a solution of standard acid. Another method is to decompose the hypochlorite with

[15] *Ger. Pats.* 188 524 and 195,896, Griesheim-Elektron.

[16] In this analysis the hydrogen peroxide should be diluted before use so as not to evolve more than 7 c c. of oxygen per c.c. of liquor, and it must be made alkaline by the addition of caustic soda until a flocculent precipitate appears The liquids in the nitrometer need not be shaken very much, and the reading should be made quickly (5 minutes after mixing), otherwise the results will be somewhat too high. Muddy solutions of bleach may be used for this test with as good results as clear liquors.

[17] Each c.c. of gas evolved reduced to 0° C and 760 mm. pressure represents 0 003167 gm. of chlorine; hence by taking 7 917 gms. of sample in 250 c c of water (= 31.67 gms per liter), and using 10 c c. of the solution for a test, 1 c.c. of gas is equivalent to 1 percent of chlorine by weight.

hydrogen peroxide, and subsequently determining the free lime by titration with acid, using phenolphthalein as an indicator.

For the titration it is advised to employ a N/10 solution of sulfuric acid. It is well to avoid an excess of hydrogen peroxide as secondary reactions take place when commercial peroxide is used, as the latter frequently contains phosphoric acid as a stabilizer and the presence of this will give a somewhat false result.

In the latter case, allowance must be made for any acid introduced with the hydrogen peroxide solution, or care should be taken to employ hydrogen peroxide solution that has been properly neutralized. The reaction with hydrogen peroxide is as follows:

$$CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2.$$

7. Testing for Free Chlorine in Fabrics.

It is sometimes required to test qualitatively for the presence of small traces of free chlorine or hypochlorite in fabrics or in solutions. There are three qualitative tests which may be conveniently applied in this connection.

(*a*) *Test with Potassium Iodide and Starch Solution.*—Free chlorine or hypochlorites liberate iodine from potassium iodide, and iodine reacts with starch to form an intense blue or blue-black color, hence small traces of chlorine or hypochlorites may be detected in this manner. The reagent is prepared by making a dilute starch paste by boiling a little starch with water and then adding a solution of potassium iodide. The reagent may be used in the form of the solution directly or potassium iodide-starch test paper is prepared by saturating filter paper with the solution and then drying and cutting up in small strips. If this test paper is dipped in a liquor or pressed on a moist piece of goods containing even small traces of chlorine a blue or black color will develop.[18]

(*b*) *Test with Potassium Iodide and Benzene*—In this case the reagent is applied by adding a small amount of potassium iodide to the liquid and shaking up with a few drops of benzene. In the presence of chlorine there will be liberation of iodine and this will dissolve in the benzene with a pale red color. By using a large quantity of the liquor all of the liberated iodine may be concentrated with a few drops of benzene, and in this manner a very small trace of chlorine may be detected.

(*c*) *Test with Toluidine Tartrate.*—A very sensitive special reagent for chlorine consists of an aqueous solution of tartaric acid and toluidine. When a drop of this reagent is added to a fabric containing the slightest trace of chlorine a dark blue color will be formed; with larger proportions of chlorine the color will change to orange. The same test may be applied to solutions containing traces of chlorine.

8. Sodium Hypochlorite.

Alkaline hypochlorites include the hypochlorites of sodium and potassium, and such preparations as "chlorozone," "chlorogene," etc.

[18] This reagent will show the same test with nitrous acid and hydrogen peroxide.

As the efficacy of these compounds in bleaching depends on the amount of available chlorine present, their valuation is carried out in the same general manner as already described under the analysis of bleaching powder. In some cases it is also required to determine the amount of alkali present, in which case the chlorine or hypochlorite must first be neutralized with an oxidizing agent and then the amount of alkali may be found by means of a titration with standard hydrochloric or sulfuric acid.[19]

According to Forster and Jofre this analysis is carried out as follows: To 50 c.c. of the alkaline hypochlorite liquor is added 5 c.c. of N/5 sodium hydrate solution, and then 10 c.c. of hydrogen peroxide solution. A few drops of phenolphthalein indicator are then added which will give a red color. The liquor is next titrated with N/5 hydrochloric acid. An exactly similar blank test is made on the hydrogen peroxide solution without the addition of the hypochlorite in order to ascertain the acid content of the peroxide. The difference between the two titrations will give the alkalinity of the hypochlorite liquor.

As with solutions of bleaching powder those consisting of sodium hypochlorite when freshly prepared may be tested for bleaching strength by the hydrometer. The ratio between the density of the solution and its content of available chlorine, however, will vary with the manner in which it is prepared and its composition. A sodium hypochlorite solution made from chlorine and caustic soda, for instance, will show a different density for the same chlorine strength than one prepared from chlorine and soda ash, and far different from one prepared by the electrolysis of salt or by reaction between soda ash and bleaching powder. With old liquors, especially of electrolytic hypochlorite, the hydrometer reading is no guidance at all.

9. Hydrogen Peroxide.

The principal compounds used in bleaching which depend on their high condition of oxidation for their action are hydrogen peroxide, sodium peroxide, and potassium permanganate.

Hydrogen peroxide has the chemical formula H_2O_2, and is prepared by dissolving barium peroxide in water acidulated with sulfuric acid. Solutions of hydrogen peroxide are the only form in which this article appears in trade. These solutions are rather unstable, the peroxide gradually decomposing with formation of water and liberation of oxygen gas.[20] The rate of decomposition is much increased by

[19] In the preparation of electrolytic bleaching liquors it is sometimes desirable to determine analytically the alkalinity of the solution. As these liquors are obtained by the electrolysis of salt solutions, they usually contain caustic soda, sodium hypochlorite together with undecomposed sodium chloride and sodium chlorate, consequently the ordinary methods of analysis are not available, as the indicators are destroyed and if hydrochloric acid is employed for the titration chlorine will be developed from the hypochlorite, and sulfuric acid will do the same and also liberate hydrochloric acid from the sodium chloride. Nitric and oxalic acids are also unavailable. Ullman (*Chem. Zeit.*, 1893, No. 67) has proposed for this purpose the use of succinic acid, and the method is carried out as follows: A measured quantity of the electrolytic liquor is titrated with an excess of standard succinic acid solution, and then heated until the odor of hypochlorous acid has disappeared; phenolphthalein is then added, and the excess of acid is titrated back with caustic soda. Succinic acid is suitable for this purpose as it is not volatile, it expels carbonic and hypochlorous acids, but not hydrochloric, and it is not affected by oxidizing or chlorinating agents.

[20] By subjecting a 95 percent solution of hydrogen peroxide to low temperatures, it crystallizes to a solid mass, which melts at 2° C. Even an 80 percent solution will give

strong light, the presence of metals or of organic matter, or of alkalies. Phosphoric acid or acetanilide is usually added to the solution in order to render it more stable. It is also said that the addition of about 2 percent of alcohol or ether or a little sulfate of quinine is a means of retarding the decomposition of hydrogen peroxide solutions.[21] Commercial hydrogen peroxide is a colorless liquid which usually contains about 3 to 3.5 percent of H_2O_2 (10 to 12 volume strength). The strength of such solutions is generally expressed in terms of volumes of available oxygen; that is, hydrogen peroxide solution of 10 volume strength would mean a solution which on decomposition will give off 10 times its volume of oxygen gas. More recently a 15 percent solution of hydrogen peroxide has appeared as a commercial article.

Analysis of Hydrogen Peroxide Solutions.—(a) Probably the best method for estimating the strength of solutions of hydrogen peroxide is by treatment with a solution of potassium iodide and then titration with sodium thiosulfate solution. Hydrogen peroxide, in acid solution, when treated with a solution of potassium iodide, liberates an equivalent of iodine, and this latter is then estimated with thiosulfate solution, using starch paste as the indicator. The test is carried out as follows: 10 c.c. of the sample are mixed with 30 c.c. of a mixture of equal volumes of water and sulfuric acid, and an excess of potassium iodide solution is added. After standing for 5 minutes, the liberated iodine is titrated with a N/10 solution of sodium thiosulfate in the manner already indicated under the analysis of bleaching powder. Each c.c. of sodium thiosulfate used is equivalent to 0.0017 gm. of hydrogen peroxide or to 0.0008 gm. of oxygen. The weight of the oxygen found in grams multiplied by the factor 697.5 will give the volume of the oxygen in c.c. and at 0° C.

(b) Another method for the analysis of solutions of hydrogen peroxide is to acidulate the sample with sulfuric acid and titrate with a N/10 solution of potassium permanganate until a faint pink color appears. Each c.c. of the potassium permanganate solution used is equivalent to 0.0017 gm. of hydrogen peroxide or to 0.0008 gm. of oxygen. The N/10 solution of potassium permanganate is prepared by dissolving 3.16 gms. of pure crystals of potassium permanganate in water and diluting the solution to 1 liter. To determine the strength of a bleach bath containing peroxide of hydrogen (or sodium peroxide), 2 c.c. of the bleach liquor are taken up in a pipette and transferred to a porcelain dish and diluted with about 100 c.c. of water. A few drops of concentrated sulfuric acid are added and then the solution titrated

crystals, if after cooling it, a crystal of hydrogen peroxide is added. This is recommended as a simple method for the preparation of anhydrous hydrogen peroxide. A few drops of liquid anhydrous peroxide dropped on moist cotton will ignite it, yet the substance itself is said to be quite stable, and if properly packed will bear transport. Bohn and Leyden have prepared hydrogen peroxide in the solid form by adding to a solution of hydrogen peroxide a quantity of gelatine and glycerin, and then cooling the mixture until a hard, solid mass is obtained. This product remains stable for a long time, and is made active by simply heating to a temperature of 75° to 100° F.

[21] It appears that the addition of crystallized naphthalene to solutions of hydrogen peroxide have the effect of retarding the decomposition of the latter to a considerable extent (see *Bull. Soc. Ind. de Mulhouse*, 1895, p. 78). Various other substances have also been tried as preservatives for solutions of hydrogen peroxide, such as boric acid, phenol, thymol, camphor, beta naphthol, formaldehyde, glycerin, zinc chloride, acetamide, acetanilide, phenacetine and tannin.

with the above described potassium permanganate solution. By observing the amount of permanganate consumed reference to the following table will show at once the strength of the bath.

C.c. of Permangante Consumed.	Equal to Real Peroxide in Gms.	Commercial Solution Equivalent to		
		Percent of Peroxide.	Percent of Available Oxygen.	Volume Strength.
0.5	0.00085	0.0425	0.021	0.14
1	0 0017	0.085	0.042	0.28
2	0 0034	0.170	0.084	0.56
3	0 0051	0.225	0.126	0.84
4	0 0068	0.340	0.168	1.12
5	0.0085	0.425	0.210	1.40
6	0.0102	0.510	0.252	1.68
7	0.0119	0.595	0.294	1.96
8	0.0136	0.680	0.336	2.24
9	0 0153	0.765	0.378	2.52
10	0.017	0.850	0.420	2.80
11	0.0187	0.935	0.462	3.08
12	0.0204	1.020	0.504	3.36
13	0 0221	0.105	0.546	3 64
14	0 0238	1.190	0.588	3.92
15	0.0255	1.275	0.630	4.20
20	0 034	1.700	0.840	5.60
25	0 0425	2.125	1.050	7.00
30	0.051	2.550	1.260	8.40
35	0.0595	2.975	1.470	9.80
40	0 068	3.400	1.680	11.20
45	0.0765	3.825	1.890	12.60
50	0.085	4.250	2.100	14.00
55	0.0935	4 675	2 310	15.40

Pentecost[22] gives the following method for the analysis of hydrogen peroxide: A 50 c.c. graduated tube, closed at one end is filled with water up to about the 28 c.c. mark, and about 1 c.c. of sulfuric acid is added; then 1 c.c. of the hydrogen peroxide to be tested is carefully added from a burette; the thumb is placed over the mouth of the tube, the latter inverted, and the volume of air read off. A few crystals of potassium permanganate, loosely wrapped in a bit of tissue paper, are then dropped into the tube, the thumb is immediately placed over the tube mouth to make it gas-tight, while the hand firmly grasps the tube and shakes it thoroughly for two to three minutes. The tube is then plunged into a glass cylinder of cold water, mouth downwards; the mixed gases are cooled to the ordinary temperature, and the volume read off. After deducting from this the volume of air-space previously ascertained, one-half the residual volume obtained represents the volume of available oxygen in the sample.

As a solution for the testing of hydrogen peroxide, Mork recommends one containing 6.625 gms. of potassium permanganate per liter. Each c.c. of this solution corresponds to 0.5 c.c. of oxygen. In testing the sample of hydrogen peroxide, 500 c.c. of water are placed in a

[22] *Jour. Soc. Chem. Ind.*, 1893, p. 327.

basin, 5 c.c. of dilute sulfuric acid are added, and sufficient of the permanganate solution to just give a reddish tinge. Then 5 c.c. of the hydrogen peroxide solution are added, and the permanganate solution run in until a permanent red color is obtained. The number of c.c. of permanganate solution used, divided by 10, gives the volume of oxygen liberated by 1 volume of the hydrogen peroxide.

Oxalic acid is frequently added as an adulterant to solutions of hydrogen peroxide, as this body will also reduce potassium permanganate, and in the analysis of the peroxide a false result would be obtained. To detect the presence of oxalic acid, about 50 c.c. of the sample are diluted with the same volume of water, then mixed with 15 c.c. of a 10 percent solution of sodium acetate and 10 c.c. of acetic acid. A small amount of a solution of calcium chloride is then added, and if no precipitate is formed, oxalic acid is absent. If a white precipitate is produced on the addition of the calcium salt, it may consist of either calcium oxalate or sulfate (as hydrogen peroxide solutions often contain sulfuric acid). The nature of the precipitate is determined by filtering off and treating it on the filter with warm dilute sulfuric acid. If the filtrate which passes through decolorizes a few drops of weak potassium permanganate solution, it indicates the presence of oxalic acid.

The stability of hydrogen peroxide solutions is an important factor in their analysis. According to Heermann,[23] a sample of good hydrogen peroxide on standing for 14 days at room temperature (65 to 75° F.) should not show a loss of more than 0.01 to 0.02 percent in content of peroxide. The presence of even small quantities of impurities in the liquid, such as pieces of cork, straw, sand, etc., will seriously impair the stability of the solution. Direct sunlight acting on the solution will cause rapid decomposition. According to Fawsitt,[24] an exposure to direct sunlight for 1 month (July) caused a loss in strength of 22 percent (in a 9 volume solution); whereas a similar sample exposed only to diffused daylight showed a loss of only 1.1 percent.

10. Sodium Peroxide.

This compound has become an important chemical for use in bleaching. It is prepared by heating metallic sodium in oxygen gas, and has the formula Na_2O_2. It occurs in trade as a yellowish white powder which rapidly absorbs moisture when exposed to the air and liberates oxygen.[25] It dissolves in water with the liberation of great heat, forming caustic soda, $NaOH$, and hydrogen peroxide, H_2O_2.[26]

[23] *Färbereichemische Untersuchungen.*

[24] *Jour. Soc. Chem. Ind.*, 1902.

[25] Stable bleaching preparations containing sodium peroxide are said to be obtained in the following manner (*Fr. Pat.* 423,949): Mix 1 part of sodium peroxide with 3 parts of rosin; this gives a very stable product. By intimately mixing with it 1 to 10 parts of ethylacetate, the rosin is gelatinized and the resulting plastic mass is decomposed by water only above a temperature of 80° C. The addition of 10 percent of soda ash in turn converts this product into a solid substance that may be powdered.

[26] Methods have been suggested for regulating the solution of sodium peroxide in water. Greener gives a method of mixing the peroxide first with a little carbon tetrachloride which coats the material and lessens its solubility so that the heat of reaction is much lowered. The carbon tetrachloride is also useful as a fat solvent in the bleaching process. Special apparatus has also been devised for the proper solution of sodium peroxide.

Analysis of Sodium Peroxide.—Archbutt[27] gives the following method for the analysis of this compound: 0.25 gm. of the sample is placed in the dry tube of a nitrometer flask, and about 5 c.c. of water containing a drop of cobalt nitrate are placed in the flask itself. The sodium peroxide is then brought in contact with the water, when rapid and complete decomposition takes place, and the volume of oxygen evolved is the available oxygen contained in the sample taken.[28]

Another method for the analysis of sodium peroxide is the following: 1 gm. of the sample is dissolved in about 500 c.c. of water containing 10 c.c. of sulfuric acid, and the solution diluted to 1 liter; 100 c.c. of the solution is withdrawn for titration, about 10 c.c. of a 20 percent solution of manganous sulfate is added, and the liquid is then titrated with N/10 potassium permanganate; each c.c. of the latter being equivalent to 0.0039 gm. of sodium peroxide, Na_2O_2.

Sodium peroxide may be qualitatively recognized by giving a blue coloration with ether on shaking with chromic acid solution. When compared with the ordinary commercial hydrogen peroxide (3 percent solution) sodium peroxide theoretically is 14.5 times as strong; but as commercial sodium peroxide is only about 93 to 95 percent Na_2O_2, and as there is some loss of oxygen in dissolving, the proportion which holds in practice between hydrogen peroxide and sodium peroxide is about 1:11.

11. Potassium Permanganate.

This is produced by fusing manganese dioxide with caustic potash in the presence of potassium chlorate. It occurs in the form of purplish black crystals readily soluble in water to a dark violet solution. The formula of potassium permanganate is $KMnO_4$ or $K_2Mn_2O_8$. It is a powerful oxidizing agent either in acid, neutral, or alkaline solutions. The solution is also an excellent disinfectant and is employed for this purpose under the name of "Condy's fluid."

Potassium permanganate is soluble in about 16 parts of water; if exposed to the light the solution soon shows a brown deposit of manganese hydrate, so it should be kept in dark colored bottles away from the light. The neutral solution has a less oxidizing power than the acid solution, as shown by the following reactions:

$$2KMnO_4 + 3H_2O = 2KOH + 2MnO_2.H_2O + 3O.$$
$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

When used as a bleaching agent, therefore, it should always be employed in an acid solution, under which circumstances the liquor will remain clear, whereas if no acid is used, a precipitate of hydrated

[27] *Analyst*, 1895, p. 3.

[28] The following is an analysis of a sample of commercial sodium peroxide:

	Percent
Sodium peroxide	90 41
Caustic soda	8 73
Alumina and iron oxide	0.49
Undetermined	0 37

This sample also contained traces of sodium carbonate, sodium chloride, sodium sulfate, and unoxidized metallic sodium. At the present time a sample of good commercial sodium peroxide should contain 95 to 98 percent of Na_2O_2.

manganese dioxide will be formed. This will be deposited on the fiber and give a brown color, which has to be subsequently removed by treatment with a second bath containing a reducing agent (sodium bisulfite or oxalic acid). Also when used without the acid the solution will contain caustic potash which is detrimental to wool and silk.

Analysis of Potassium Permanganate.—As this salt decomposes oxalic acid, a convenient means for its analysis is to titrate its solution with a standard solution of oxalic acid. The method is carried out as follows: 3.16 gms. of the sample of potassium permanganate are dissolved in water and the solution diluted to 1 liter; 100 c.c. of this solution are withdrawn and titrated with N/10 oxalic solution with the addition of a few drops of sulfuric acid to prevent the precipitation of manganese hydrate. The number of c.c. of oxalic acid solution required correspond to the percentage of potassium permanganate present in the sample. The N/10 solution of oxalic acid is prepared by dissolving 6.301 gms. of pure oxalic acid crystals ($C_2H_2O_4.2H_2O$) in water and diluting the solution to 1 liter.

12. Perborate Compounds.

Sodium perborate has the chemical formula $NaBO_3$, but the commercial perborate compounds to be met with are seldom pure sodium perborate. The oxygen content of these compounds varies with the degree of purity and the amount of water of crystallization. The pure crystalline salt has 4 molecules of water of crystallization and corresponds to an active oxygen content of 10.4 percent. Sodium perborate readily dissolves in acidulated water without loss of oxygen. The cold solution is quite stable but when heated to 95° F. oxygen gas is evolved. In the presence of catalyzing substances, such as iron or copper, the decomposition is more rapid even at lower temperatures. The solution of perborate in water reacts weakly alkaline. It may be further stabilized by the addition of sodium phosphate or similar salts.

The acidulated solution of sodium perborate gives the same qualitative reactions as hydrogen peroxide, for, indeed, it consists of a solution of hydrogen peroxide and borax. It gives a blue coloration when shaken with ether and chromic acid solution. It also gives the boric acid reaction, giving a green flame when dissolved in alcohol and sulfuric acid and burned.

The bleaching value (content of active oxygen) of sodium perborate or its compounds (Ozonite, Clarax, Persil, Perborin, etc.), is determined in the same manner as with hydrogen peroxide, most conveniently by titration with a standard solution of potassium permanganate, or by the iodometric method. The latter is said to yield the most satisfactory results. In the case of soap powders, however, containing perborate it is necessary to previously remove the soap. A method which may be used directly with a soap powder and perborate mixture consists in treating the solution with a sodium hypochlorite solution in a nitrometer and measuring the volume of the liberated oxygen. The results obtained are in agreement with those obtained by the iodometric method. The titration of perborates with permanga-

nate is said not to be very reliable, though the best results are obtained by adding a slight excess of the perborate solution to a definite volume of the permanganate solution acidified with sulfuric acid, and then titrating the excess with permanganate. The titration should also be carried out at 15 to 20° C., and the acid concentration should be 5 percent of sulfuric acid on the total volume. The determination of perborates by the gasometric method by decomposition with permanganate is untrustworthy.[29]

[29] Trickett, *Analyst*, 1920, p. 88.

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